

AN ABSTRACT OF THE THESIS OF

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Title: INTRAMOLECULAR TRANSFER OF COMPLEXED RADICALS
AS A POSSIBLE EXPLANATION FOR LONG-RANGE
SUBSTITUENT EFFECTS OBSERVED IN HYDROGEN
ABSTRACTION REACTIONS

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Gerald Jay Gleicher

The relative rates of hydrogen abstraction from 1-phenylalkanes and α,ω -diphenylalkanes using N-bromosuccinimide and bromotrichloromethane were determined at 70°C. In both cases the reactions were photoinitiated. Only benzylic bromination was observed. The 1-phenylalkanes reacted with both reagents to give rates largely independent of substrate. Similarly, the rate of the reaction between the α,ω -diphenylalkanes and bromine atom showed little dependence on substrate structure. However, for the reaction of the α,ω -diphenylalkanes with trichloromethyl radical, the rates were strongly dependent upon the structure of the substrate. A maximum was found for 1,6-diphenylhexane. These last results suggest the possibility of hydrogen abstraction by a route where the radical is first complexed

with the aromatic ring at one end of the substrate and then intramolecularly transferred to the site of hydrogen abstraction at the opposite end of the substrate.

The relative rates of hydrogen abstraction from 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes by trichloromethyl radical were also determined under the same conditions. Application of the Hammett equation yielded a rho value of -0.40 for this reaction. Application of the Taft equation yielded rho values of -1.34 or -1.54 depending upon the Taft substituent constants used. The results for both the Hammett and Taft equations suggest a significant long range substituent effect.

To explore the source of this effect, the relative rates of hydrogen abstraction from 4-phenyl-1-substitutedbutanes by trichloromethyl radical were also determined. Application of the Taft equation yielded a rho value of only -0.32. This substituent effect probably arises from inductive interactions between the substituent and the transition state of hydrogen abstraction.

The large difference between the Taft rho values obtained for the reaction of the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes and the 4-phenyl-1-substitutedbutanes with bromotrichloromethane suggest an additional mechanism operative in the former system. A significant amount of that reaction may follow a path where the abstracting :

radical first forms a pi complex with the substituted phenyl ring of the substrate and then is intramolecularly transferred to the site of hydrogen abstraction.

Intramolecular Transfer of Complexed Radicals as a
Possible Explanation for Long-Range Substituent
Effects Observed in Hydrogen Abstraction
Reactions

by

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To My Parents

and

Mary Ann

Christ is both the first
principle and the upholding
principle of the whole scheme
of creation.

Colossians 1:17
(J.B. Phillips)

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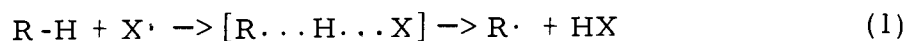
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INTRAMOLECULAR TRANSFER OF COMPLEXED RADICALS
AS A POSSIBLE EXPLANATION FOR LONG-RANGE
SUBSTITUENT EFFECTS OBSERVED IN
HYDROGEN ABSTRACTION REACTIONS

INTRODUCTION

Hydrogen abstraction is one of the most common radical reactions. Much effort has gone into trying to understand the factors that determine the reactivities of both the radical and the hydrogen donor. Thermodynamic, electronic, steric, and solvent effects have been used to explain the observed differences in reactivity (1, 2, 3).

In a typical hydrogen abstraction, shown in Equation 1, the transition state has the H-X bond partly formed and the R-H bond of the hydrogen donor partly broken.



Production of a strong H-X bond or the destruction of a weak R-H bond should promote a facile hydrogen transfer.

The reactivity of the hydrogens of aliphatic hydrocarbons toward the hydrogen abstraction reaction decreases in the order tertiary > secondary > primary (4). This order is expected and is inverse to the bond energies involved (4). In reaction with methane the closely related series of radicals fluorine atom, chlorine atom, and bromine atom give an order of reactivity paralleling the strength

of the developing hydrogen halide bond (4). Both these results can be explained by a thermodynamic approach relating reactivity to the overall change in the enthalpy of the reaction. This approach is, however, limited. Hydrogen atom, chlorine atom, and trifluoromethyl radical should form bonds of comparable strength with hydrogen. Common substrates reacting with these three species, however, show vastly different reactivities (4).

The selectivity and reactivity of a radical can frequently be related. The more reactive a radical is the smaller its energy of activation and the less selective it should be. Hydrogen abstraction by the more reactive radical will be highly exothermic. The highly selective radical will have a large energy of activation and its hydrogen abstraction reaction will be more endothermic.

Hammond's postulate suggests that the transition state for an exothermic reaction will resemble reactants, with little bond breaking, while the transition state for an endothermic reaction will resemble products (5). These ideas are illustrated in Figure 1. For endothermic reactions reactivity would be promoted by factors that stabilize the developing radical. For exothermic reactions the characteristics of the hydrogen donor and the attacking radical would determine reactivity.

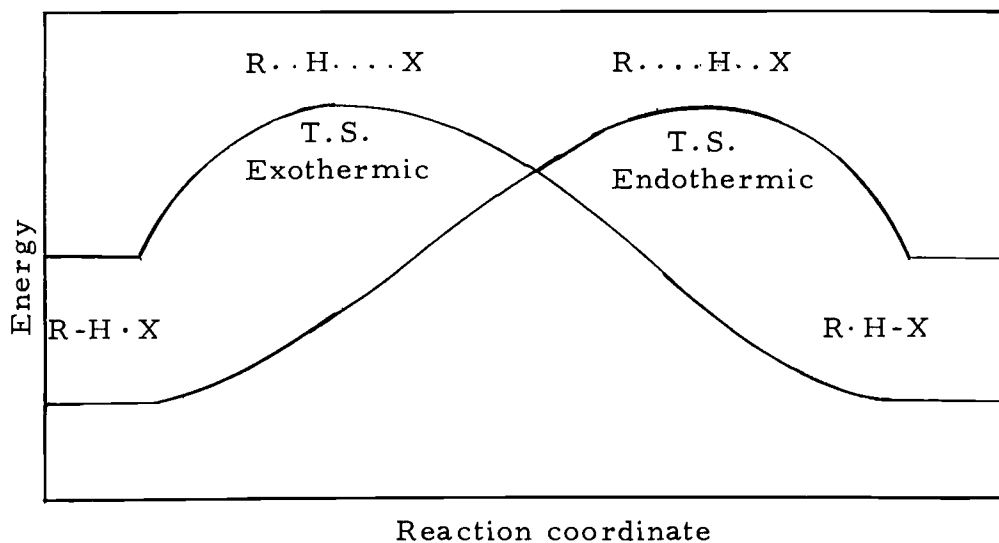


Figure 1. The Hammond postulate.

The transition state for the hydrogen abstraction reaction can be thought of as a resonance hybrid of structures A, B, C, and D shown in Figure 2.

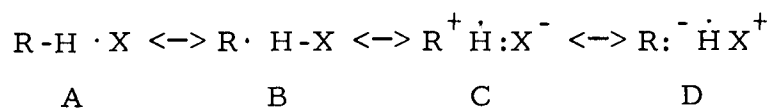


Figure 2. Transition state for hydrogen abstraction.

For very exothermic reactions structure A best describes the transition state while in more endothermic reactions the transition state could be represented by an important contribution from form B. The ionic structures would be most important for hydrogen abstraction by a very electrophilic or very nucleophilic radical.

The usefulness of these ideas is illustrated in understanding the relative rates of hydrogen abstraction for unsubstituted arylmethanes by the very reactive tert-butoxy radical and the less reactive trichloromethyl radical. The relative reactivities of these arylmethanes could be correlated with the change in pi binding energy between the incipient arylmethyl radical and the starting hydrocarbon as calculated by the SCF approach for the more endothermic reaction with trichloromethyl radical (6). No such correlation was found for abstraction with the more reactive t-butoxy radical. For the trichloromethyl radical the transition state was much like the product. Resonance structure B in Figure 2 must, therefore, make a substantial contribution to the transition state. The change in pi binding energy between reactant and product was closely paralleled by the energy of activation for the reaction. Thus, this change determined the relative reactivities. This, of course, is the essence of the well-known Polanyi relationship (7).

The importance of electronic effects in understanding hydrogen abstraction is clearly shown by the difference in the relative reactivities of cyclohexane and toluene toward photobromination and photochlorination. Russell and Brown found that at 80°C a hydrogen atom of cyclohexane is 0.004 times as reactive as a benzylic hydrogen of toluene toward bromine atom (8). Toward chlorine under the same conditions the cyclohexane hydrogen is 2.8 times more reactive than

a benzylic hydrogen in toluene (8). Reaction with bromine is less exothermic than the same reaction with chlorine. Hydrogen bromide has a bond dissociation energy of only 87 kcal per mole while hydrogen chloride has a bond dissociation energy of 103 kcal per mole. In photobromination the transition state will resemble the products more than in photochlorination. Reaction of bromine atom with toluene will, therefore, be favored over reaction with cyclohexane principally because the developing benzylic radical can be stabilized by resonance with the benzene ring of toluene. In photochlorination the transition state will tend to resemble reactants. Since there is little bond breaking, differences in resonance stabilization will be of small importance. Reaction with cyclohexane will be favored since the methylene groups next to the site of attack can donate electrons inductively to increase the electron density at the site of attack by the electrophilic radical. By induction a phenyl group is electron withdrawing and so will decrease the electron density in the carbon hydrogen bonds of the methyl group of toluene. Both chlorine atom and bromine atom are electrophilic species. The polar contributing form C in Figure 2 should make a contribution to the energetics for both reactions.

Further evidence that the rate of hydrogen abstraction is influenced by electronic effects is suggested by the fact that the relative reactivities of substituted toluenes toward hydrogen abstraction

can be correlated with the Hammett equation (9, 10). The form of this equation is shown below.

$$\log k/k_o = \rho \sigma \quad (2)$$

For reactions where there is the possibility of direct delocalization of electrons from the substituent through the aromatic ring to the site of reaction, such as in hydrolysis of substituted cumyl chlorides, use of a different set of substituent constants, sigma plus, has been proposed by Brown and Okamoto (11).

Table 1 shows a brief summary of rho values for hydrogen abstraction from substituted toluenes. These rho values can be explained by assuming rho will be dependent on the structure of the transition state and the electronegativity of the radical. Since the data were obtained at different temperatures and in different solvents the rho values cannot be directly compared. However, since hydrogen transfer is approximately isoentropic, the rho value for a given radical will always have the same sign but will decrease in absolute value as the temperature is raised (12).

The relationship between rho and the extent of radical development in the transition state can be illustrated by comparing the results of benzylic hydrogen abstraction by bromine and chlorine atoms. Both of these species are highly electronegative with chlorine atom being somewhat more electronegative than bromine atom. It might be

Table 1. Rho values for hydrogen abstraction from substituted toluenes.

Radical	Temp. °C	Solvent	Rho Sigma	r ^(a)	Rho Sigma Plus	r ^(a)	References
$\underline{t}\text{-C}_4\text{H}_9$	30°	thiol	+0.99	0.96	--	--	12
CH ₃	100°	CCl ₄	-0.121	--	-0.136	--	13
C ₆ H ₅	60°	CCl ₄	-0.4	--	-0.3	--	14
$\underline{t}\text{-C}_4\text{H}_9\text{O}$	50°	C ₂ Cl ₃ H and CF ₂ Cl -CFCl ₂	-0.41	0.987	-0.35	0.974	15
Cl	60°	CCl ₄	-0.48	0.997	--	--	16
Br	80°	CCl ₄	-1.68	0.945	-1.38	0.977	17
CCl ₃	50°	BrCCl ₃	--	--	-1.46	--	18

(a) Correlation coefficient.

expected that rather large absolute values for ρ would be found for both these radicals with the absolute value for abstraction by chlorine somewhat larger than that for abstraction by bromine. Correcting for temperature, a large difference in the ρ values for these processes can be seen. The latter case, abstraction with bromine atom, shows the larger absolute value. This result can be explained by saying that chlorine atom is much more reactive than bromine atom. Thus the transition state is structurally much closer to reactants. With bromine there is much more bond breaking in the transition state and the substituents will be more effective in influencing the relative stabilities of the incipient radicals. In the case of hydrogen abstraction with chlorine atom the contribution from structure A in Figure 2 best describes the transition state while for bromine atom resonance forms B and C are much more important.

This dependence on the degree of radical formation also suggests that very reactive radicals like chlorine atom might best correlate with σ (19) since changes in the electron density of the carbon-hydrogen bond is the main mechanism by which the substituents could influence the rate. Less reactive radicals like bromine would correlate with σ^+ (19) since more bond breaking could well be associated with a greater degree of electron transfer in the transition state. The data on hydrogen abstraction is contradictory concerning these ideas (12-18).

Primary deuterium isotope effects also support the idea that the key difference between hydrogen abstraction with bromine atom or chlorine atom, as reflected in their rho values, arises from differences in the transition state. In closely related reactions the larger the ratio of k_H/k_D the more symmetric the transition state (20). As can be seen in Table 2 bromine atom shows a larger deuterium isotope effect than chlorine. This suggests more bond breaking in the transition state for hydrogen abstraction with bromine than for chlorine.

Table 2. Primary deuterium isotope effects in hydrogen abstraction from toluene.

Radical	k_H/k_D	Temperature	Ref.
Chlorine atom	1.30 ± 0.01	77°C	21
Bromine atom	4.86 ± 0.03	77°C	21
Phenyl radical	4.5 ± 0.5	60°C	22

The polar influence on rho is suggested by data in Tables 1 and 2. Bromine atom has a rho value with an absolute value much larger than phenyl radical yet deuterium isotope effects are similar. The similar deuterium isotope effects suggest a similar amount of bond-breaking in the transition state so the difference in rho could reflect the different amount of positive charge built up in the transition state. Thus bromine atom would be considered a more electronegative radical than phenyl.

A most conclusive illustration of the polar influence on ρ is shown in the results for hydrogen abstraction by t-butyl radical (12). Here the radical itself can stabilize positive charge in the transition state. Resonance form D in Figure 2, showing a buildup of positive charge on the radical and a buildup of negative charge on the substituted toluene substrate, would thus make an important contribution to describing the transition state. Electron withdrawing groups on toluene would stabilize the buildup of negative charge so a positive ρ value would be expected and is observed (12).

For a given radical the absolute value of ρ should decrease as hydrogen is abstracted from more reactive hydrogen donors because the transition state should increasingly resemble the reactants. Data in Table 3 shows this to be true for bromine atom. With a more reactive donor both the absolute value of ρ and the deuterium isotope effect decreases.

Table 3. Dependence of ρ and deuterium isotope effect on reactivity for hydrogen abstraction from α - and α, α -substituted toluenes.

	Relative Reactivity 40° C	k_H/k_D 77° C	Rho Plus
Toluene	1 (21)	4.86 (20)	-1.35 at 80° C (23)
Ethylbenzene	20 (21)	2.67 (20)	-0.53 at 80° C (24)
Cumene	40 (21)	1.81 (20)	-0.29 at 70° C (25)

The Hammett equation has been useful in determining the identity of the chain-propagating radical in bromination reactions with N-bromosuccinimide. The accepted mechanism is shown in Figure 3. Molecular bromine, N-bromosuccinimide, N-bromotetrafluoro-succinimide, N-bromotetramethylsuccinimide, and several other N-bromoamides showed similar rho values for reaction with substituted toluenes (23, 27). This would suggest that all these reagents have a common hydrogen abstracting agent, bromine atom.

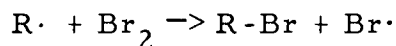
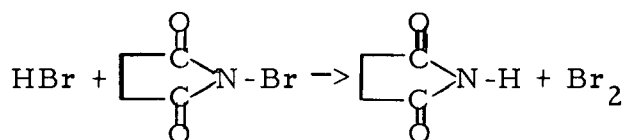
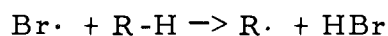


Figure 3. The mechanism for bromination with N-bromosuccinimide (17, 23, 26, 27).

Different rho values for reactions of substituted toluenes with N-bromosuccinimide (17) and bromotrichloromethane (18) as well as somewhat different selectivities toward several aralkyl hydrocarbons (28) has suggested the following mechanism for bromination with bromotrichloromethane.

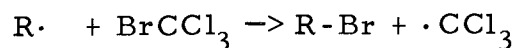


Figure 4. The mechanism for bromination with bromotrichloromethane (18).

Both the mechanism in Figure 3 for bromination with N-bromosuccinimide and the mechanism in Figure 4 for bromination with bromotrichloromethane have been recently questioned (29, 30).

In aliphatic systems where resonance effects may be neglected, Taft has suggested that Equation 3 should be followed (31).

$$\log(k/k_0) = \rho^*\sigma^* \quad (3)$$

k/k_0 is the relative rate of the substituted compound to the standard. Sigma star, the substituent constant, describes the electron donating or withdrawing properties of the substituent relative to methyl. The rho value shows the dependence of the relative rates of the given reaction on the polar effects.

The relative rates of hydrogen abstraction by several electrophilic radicals have been correlated with the Taft equation. Photochlorination in the system $\text{H-CH}_2\text{-X}$ where X was various alkyl, chloroalkyl, and cyanoalkyl groups gave rho of -0.85 at 40°C (32). The same system gave a rho of -0.69 for the tert-butoxy radical (33). Photochlorination of several aliphatic esters, acids, and nitriles gave

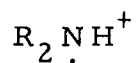
a rho of -0.2 at 100°C (34). t-Butoxy radical reacted with substituted cyclohexanes at 135°C giving relative rates that could be correlated with the Taft equation to give rho of -0.4 (35).

The rate of hydrogen abstraction from 1-substituted adamantanes at 40°C with bromine atom gave rho of -0.59 with correlation coefficient of -0.992 (36). The same reaction with trichloromethyl radical gave rho of -0.40; correlation coefficient of -0.980 (37). In both of the last two cases the rigidity of the adamantane system allowed the data to be correlated with a field effect model using the Kirkwood-Westheimer approach. This approach allowed an estimation of the amount of charge developed in the transition state. With bromine atom 0.17 of a positive charge was developed in the transition state while with trichloromethyl radical the value was 0.12 of a positive charge.

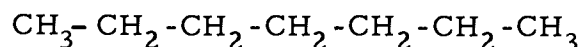
Steric effects on the rates of hydrogen abstraction have also been observed. The tertiary hydrogens in 2,4-dimethylpentane and in 2,2,4-trimethylpentane might be expected to be more reactive than the tertiary hydrogen in 2-methylpropane. Development of the planar product would remove some of the unfavorable nonbonded interactions in the reagent. A decrease of such nonbonding interactions in the transition state would increase the reactivity. The tertiary hydrogens in 2,4-dimethylpentane toward hydrogen abstraction by phenyl radical were, however, less reactive than normal tertiary hydrogens (38).

The tertiary hydrogens in 2,4-dimethylpentane and in 2,2,4-trimethylpentane were also less reactive than normal tertiary hydrogens toward hydrogen abstraction by free chlorine atom in carbon tetrachloride (39). These results would suggest that there is little bond breaking in the transition state so there would be little decrease of nonbonded interactions in the reactant molecule. In the most stable conformation of these molecules the tertiary hydrogens may be shielded from attack of the abstracting radical.

Minisci and co-workers studied hydrogen abstraction from heptane by dialkylammonium radical cations (40). The isomer



distribution for abstraction of hydrogen from heptane by radicals generated from protonated N-chlorodimethylamine or N-chlorodiisobutylamine were:



$$1.1 \quad 55.6 \quad 29.0 \quad 14.3 \quad \text{R} = \text{CH}_3$$

$$1.3 \quad 64.4 \quad 29.9 \quad 11.3 \quad \text{R} = \text{i-C}_4\text{H}_9$$

These results suggest that the hydrogens bonded to carbon 2 are much more reactive than the hydrogens bonded to carbon 3. This difference in reactivity increases as the steric bulk of the alkyl groups in the radical is changed from methyl to isobutyl. The radicals formed on

carbon 2, 3, or 4 should be of about equal electronic stability. The best explanation for these results is that the hydrogens on the penultimate position of heptane are less sterically hindered than those on the internal positions.

The trichloromethyl radical may be particularly sensitive to steric hindrance. Data for hydrogen abstraction from relatively unhindered positions, such as the benzylic carbon of substituted toluenes (17, 18), ethylbenzenes (41, 42), and α -methoxytoluenes (43) as well as the 1-position of substituted adamantanes (36, 37), suggest that the bromine atom is inherently more selective than the trichloromethyl radical. In contrast trichloromethyl radical was found to be more selective than bromine atom for hydrogen abstraction from cumene (44) and neopentylbenzene (45). This difference in selectivity may be caused by unfavorable steric interactions in the transition state between the large attacking radical and the alkyl groups adjacent to the active site in the substrate. These steric interactions can lead to more carbon-hydrogen bond breaking in the transition state thus increasing the sensitivity of the reaction to electronic effects of the substituents.

Eghdami and Gleicher reacted a series of eight α -alkyltoluenes and α, α -dialkyltoluenes with trichloromethyl radical at 70° C (46). The relative reactivity of these compounds could be correlated with the following equation giving a correlation coefficient of 0.980.

$$\log k_{\text{hydrocarbon}}/k_{\text{cumene}} = -5.777 \Sigma\sigma^+ + 0.850 \Sigma E_s - 3.748 \quad (4)$$

Both the electronic and steric parameters refer to the group(s) in the alpha position.

The rates of free radical reactions are sensitive to medium effects as well as substituent effects. Russell first showed the importance of complexation of free radicals on the selectivity of hydrogen abstraction (47, 48). He found that the solvent had a very large effect on the products of chlorine atom attack on 2,3-dimethylbutane. In most aliphatic solvents, a tertiary hydrogen of 2,3-dimethylbutane is three or four times more reactive than a primary hydrogen toward abstraction by chlorine atom. Aromatic solvents, however, have a pronounced effect upon the relative reactivity of the two kinds of aliphatic protons. This solvent effect increases with concentration of the aromatic hydrocarbon and with decreasing temperature. The solvent effect is small for aromatic compounds such as nitrobenzene containing an electron withdrawing substituent and large for aromatic compounds such as tert-butylbenzene substituted with electron donating groups. The action of the aromatic solvents suggests that a complex between solvent and chlorine atom is formed that decreases the reactivity of the chlorine atom and increases its selectivity. Both a sigma and a pi complex suggest themselves as possible intermediates. No addition products such as chlorobenzene are found when benzene

is used as the solvent for chlorination. This would seem to rule out a sigma complex since some of the sigma complex formed would probably collapse to chlorobenzene. The intermediacy of a pi complex is suggested by a linear relationship between the logarithm of the ratio of abstraction of tertiary versus primary hydrogens and the meta sigma substituent constants for the various benzenoid solvents.

The pi complex is a charge transfer complex. Mulliken suggested representing this type of complex as a resonance hybrid of form A, the "no-bond" structure, and form B, the form where an electron has been transferred from the donor, benzene, to the acceptor, chlorine atom (49, 50). The no-bond structure is held together by weak electrostatic interactions. In valence bond theory

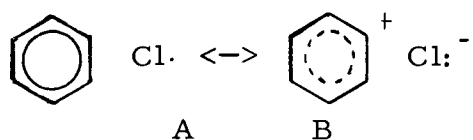


Figure 5. The pi complex of benzene and chlorine atom.

the wave function of the complex is taken as a combination of the wave functions from A and B, ψ_A and ψ_B respectively. This type of

$$\psi_{\text{charge transfer}} = a\psi_A + b\psi_B \quad (5)$$

complex often shows an intense absorption band which corresponds

to an electronic transition from the ground state of the complex where the form A best describes the pi complex to an excited state where form B is more important. Both the bonding energy of the complex and the energy for the electronic transition to the excited state depend upon the ionization potential of the donor and the electronic affinity of the acceptor.

There is direct evidence that halogen atoms can form pi complexes with aromatic donors. Pulse radiolysis of pure bromobenzene or flash photolysis of dilute solutions of bromine in bromobenzene produced a short lived bromine atom-bromobenzene complex (51). This complex could be detected from an absorption band centered at 560 nm. The intensity of the absorption at 560 nm was found to decrease with increasing concentration of added triphenylmethane. This would suggest that after formation the bromine atom can either complex with bromobenzene or abstract hydrogen from triphenylmethane.

Walling has suggested that the aromatic solvent may make changes both in the activation energy and the entropy of the hydrogen abstraction reaction (52). Russell's explanation suggests that solvent complexation stabilizes the abstracting radical and thus increases the activation energy for the reaction. This approach neglects any entropy effects. Studies of solvent effects on the selectivity of hydrogen abstraction over a wide temperature range would allow the relative

importance of changes in both activation energy and entropy to be determined.

Hradil and Chvalovsky examined the effects of different aromatic solvents on the relative rates of hydrogen abstraction by chlorine and bromine atoms from substituted toluenes (53). They found little dependence of relative rates on changes in temperature between 60° and 80°C. The rho values found for chlorination of substituted toluenes in different solvents were linearly dependent on the meta sigma constants of the substituents of the aromatic solvent. The absolute value of rho decreased with the decreasing ability of the solvent to donate electrons for formation of a pi complex. Thus, as in Russell's work, selectivity is related to the extent of pi complexing.

Other parts of Hradil and Chvalovsky's work do not completely agree with Russell's findings. The rho values found for bromination of substituted toluenes in different aromatic solvents were best correlated with the sigma plus constants of the substituents of the solvents. In the case of chlorination of substituted toluenes in benzene, as well as the corresponding bromination in a series of aromatic solvents, the apparent absolute rates of reaction increase with the increasing selectivity of the reagent. The usefulness of this study is lessened because compounds with highly electron donating substituents, either as substrates or as solvents, were not used. These kinds of compounds should be most reactive to hydrogen abstraction and to pi

complexation. The authors suggest no explanation for their data except that pi complexation of the abstracting agent with the solvent is not the single factor determining selectivity and reactivity.

Martin and Gleicher studied the addition of trichloromethyl radical to 3-phenyl-1-propenes and 4-phenyl-1-butenes (54). In these systems the substituted phenyl ring is insulated from the radical carbon atom generated by the reaction. Substituent effects would hence be expected to be small. Hammett rho values of -0.29 for 3-(substitutedphenyl)-1-propenes and -0.20 for 4-(substitutedphenyl)-1-butenes were found. The rho values are rather large for this type of reaction. The addition of the trichloromethyl radical to substituted styrenes under comparable conditions showed a substituent effect of only -0.48 (55). Insulation of the aromatic portion of the system from the site of radical formation by one or two methylene groups should have markedly lessened this dependence.

Several explanations might be advanced for these rho values. Perhaps a bridged radical, analogous to a phenonium ion, could result in resonance stabilization of the intermediate. This seems unlikely since a good correlation with sigma is obtained with no deviation for strongly electron donating groups. A pure inductive effect seems unsatisfactory since the intervening methylene groups would insulate to give a smaller rho value of perhaps -0.1. A much larger decrease in the absolute value of rho would be expected for 4-phenyl-1-butenes

relative to 3-phenyl-1-propenes. Addition of trichloromethyl radical to 3-substituted-1-propenes and 4-substituted-1-butenes gave rho values of -0.15 and -0.06 respectively for a Hammett Taft plot (56).

The best explanation for these data seems to be that trichloromethyl radical is complexed by the aromatic system in an equilibrium step prior to transfer and addition to the double bond. The observed polar effect is a consequence of the influence of the substituent on this equilibrium preceding reaction at the double bond. Since complexation is favored by high electron density in the aromatic pi system a negative rho value is observed.

Further support for the above explanation is found in the dependence of the rate of trichloromethyl addition on the distance between the double bond and the terminal phenyl group in a series of ω -phenyl-1-alkenes (57). The rate of addition is maximum for 4-phenyl-1-butene. In this case there are three intervening carbon atoms between the phenyl group and the site of addition. The rate then decreases with a further increase in the number of carbon atoms between these two sites. This difference in rate of addition reflects the relative tendencies of the side chains of different lengths to adopt conformations which bring the double bond near the internally complexed trichloromethyl radical. This is best achieved for 4-phenyl-1-butene. With longer chain-lengths an increasing number of conformations are possible which statistically disfavor intramolecular transfer.

Russell, Ito, and Hendry explored the possibility of complexation of chlorine atom followed by intramolecular transfer of chlorine to the site of hydrogen abstraction (58). The relative amounts of chlorination in the four positions of 1-phenylbutane were measured as a function of concentration and solvent identity. Since the ratio of hydrogen abstraction from carbon 2 and carbon 3 of the alkyl chain was nearly constant under all conditions, intramolecular reactions of complexed chlorine atom with alkyl side chains were not deemed important in this system.

Martin and Gleicher found that the rate of both the hydrogen abstraction reaction and the addition reaction of trichloromethyl radical with ω -phenyl-2-methyl-2-alkenes was dependent on the length of the side chain (57). They suggested that these results could be evidence for radical complexation followed by intramolecular transfer of the radical to site of hydrogen abstraction or addition.

In molecules where radicals can be formed in the position delta to a double bond cyclization may occur. The radical may add to either end of the double bond. This would produce a cyclohexane or alkylcyclopentane system. In systems where the radical has little or no resonance stabilization the cyclopentane product is favored (59, 60, 61). Electron spin resonance studies of the products of the photolysis of 6-hexenyl peroxide at low temperature shows the spectrum of the 5-hexenyl radical. At higher temperatures only the spectrum of the

cyclized product, the cyclopentylmethyl radical, is observed (62).

As the stability of the radical in the delta position to the double bond increases the yield of the cyclohexane ring products increase. Julia (59) and Walling and Cioffari (63) suggest that cyclopentane ring formation is more rapid but the product cyclopentyl radical may equilibrate to the more stable cyclohexane isomer. This reversibility of the cyclization step is favored by stabilization of the aliphatic radical.

Radicals formed on a carbon separated from an aromatic ring by three methylene groups may cyclize (64). Intramolecular addition to an aromatic ring appears to be a less favored process than intramolecular addition to a double bond (64).

The extent of cyclization is dependent upon how good a chain transfer agent is present. The 3-(1-phenylcyclopropyl)propyl radical was produced at 120°C in benzene solution and in carbon tetrachloride solution (65). In both cases a mixture of products was obtained. In benzene solution products from intramolecular addition by the radical to the phenyl ring were produced as 42% of the isolated products. In carbon tetrachloride solution products from the intramolecular addition of the radical to the phenyl ring were produced as only 2% of the isolated products. The main product resulted from chlorine abstraction from carbon tetrachloride by the 3-(1-phenylcyclopropyl)propyl radical.

DISCUSSION OF THE PROBLEM

As has been stated, Russell (48) and Hradil and Chvalovsky (53) have shown that the selectivity of chlorine atom toward hydrogen abstraction could be correlated with the sigma meta substituent constants of the substituted aromatic compounds used as the solvent for the chlorination. Similar results have been found for hydrogen abstraction with bromine. In bromination, selectivity could be correlated with the sigma plus para constants of the substituted aromatic compounds acting as solvent for the reaction (53). These data for both chlorination and bromination suggest that the abstracting radical forms a pi complex with the aromatic solvent. Complexation of the radical increases its selectivity. The electron density of the aromatic ring will determine the stability of the pi complex and thus the selectivity of the abstracting species.

Martin and Gleicher have suggested that pi complexation of trichloromethyl radical followed by intramolecular transfer of the radical to site of addition could explain the long range substituent effects they observed for radical addition to 3-substituted phenyl-1-propenes and 4-substituted phenyl-1-butenes (54).

Russell investigated the possibility of an intramolecular reaction of complexed chlorine atoms with the alkyl side chain of butylbenzene (58). He found little change in the ratio of 2-chloro-1-phenylbutane

to 3-chloro-1-phenylbutane when the concentration or the solvent was changed. It was concluded that complexation followed by intramolecular reaction was unimportant for this reaction. It is difficult to judge the significance of this result. Chlorine atom is a very reactive, unselective abstracting agent. Chlorination takes place in all four alkyl positions. The most reactive site is the benzylic carbon. The two other methylene positions are in different electronic environments. Perhaps a longer chain length between the aromatic moiety and the reactive site is necessary in order to observe complexation and transfer. The amount of 4-chloro-1-phenylbutane produced, it should be noted, was dependent on both concentration and solvent.

A study of the possibility of radical complexation and intramolecular transfer to site of hydrogen abstraction, lacking some of the problems inherent in the chlorination of butylbenzene, is herein described. Hydrogen abstraction from α,ω -diphenylalkanes by trichloromethyl radicals and bromine atoms will be investigated. These two radicals are less reactive and more selective than chlorine atoms. Reaction should only take place in the benzylic position. The distance between the site of complexation and the site of hydrogen abstraction can be varied in a logical fashion as the number of methylene groups between the two phenyl moieties is increased. Reaction by a pathway where the radical is complexed and then intramolecularly transferred to the site of hydrogen abstraction could be

detected if a relation could be found between the relative rate of hydrogen abstraction and the number of methylene groups in the α,ω -diphenylalkanes.

The possibility of substituent effects on initial complexation of the trichloromethyl radical with an aromatic ring followed by an intramolecular transfer of the radical to site of hydrogen abstraction can also be studied. The relative rates of reaction of 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes relative to diphenylmethane can be obtained. The trichloromethyl radical should only attack the benzylic position, carbon 1, on the opposite end of the molecule from the substituted phenyl group.

The results of these studies should allow an estimation to be made of the importance of possible pi complexation of a radical followed by its intramolecular transfer to the site of hydrogen abstraction. It is anticipated that the trichloromethyl radical should be somewhat more selective than bromine atom in these studies.

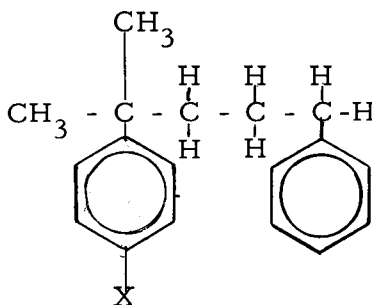
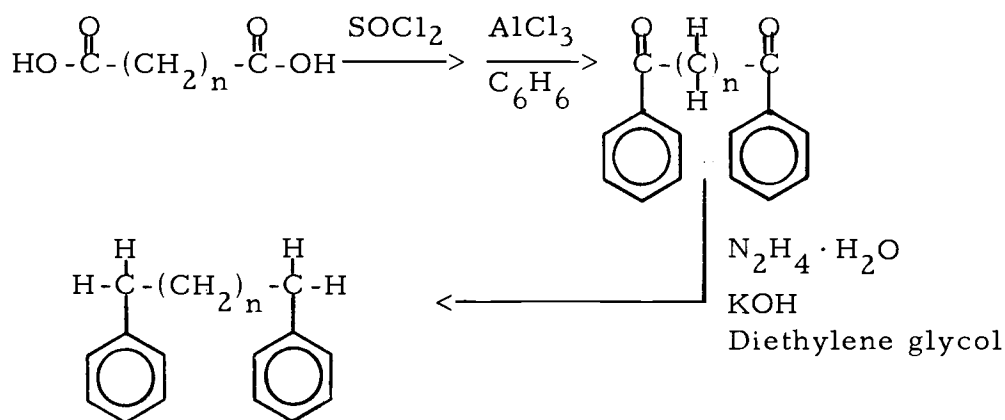


Figure 6. 4-Methyl-1-phenyl-4-(substitutedphenyl)pentane.

RESULTS AND DISCUSSION

Preparation of the Compounds

The α,ω -diphenylalkanes were synthesized by standard reactions. Most of these compounds were prepared by the sequence shown in Synthetic Scheme 1.

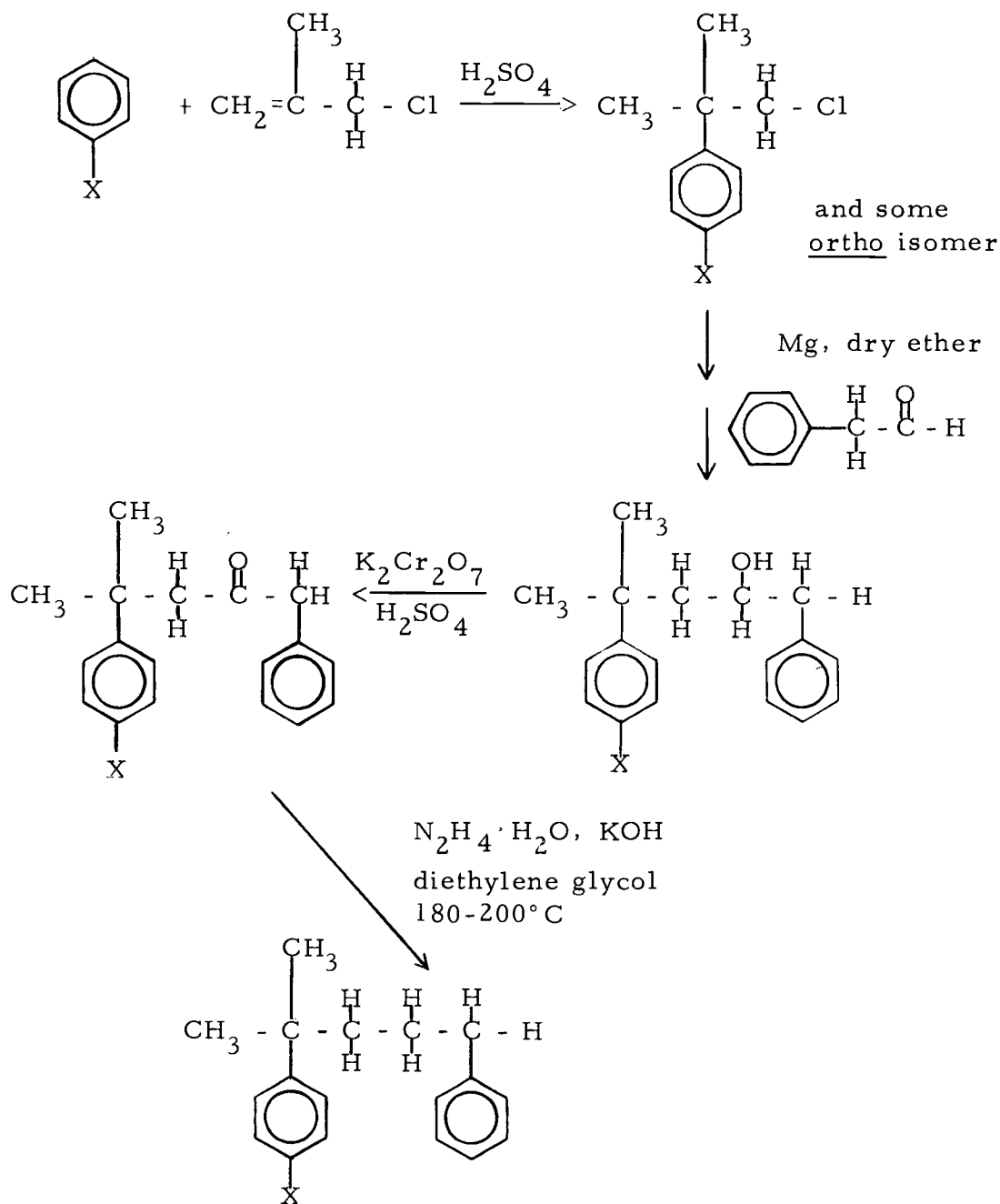


Synthetic Scheme 1. Synthesis of α,ω -diphenylalkanes where $n = 3, 5-8$.

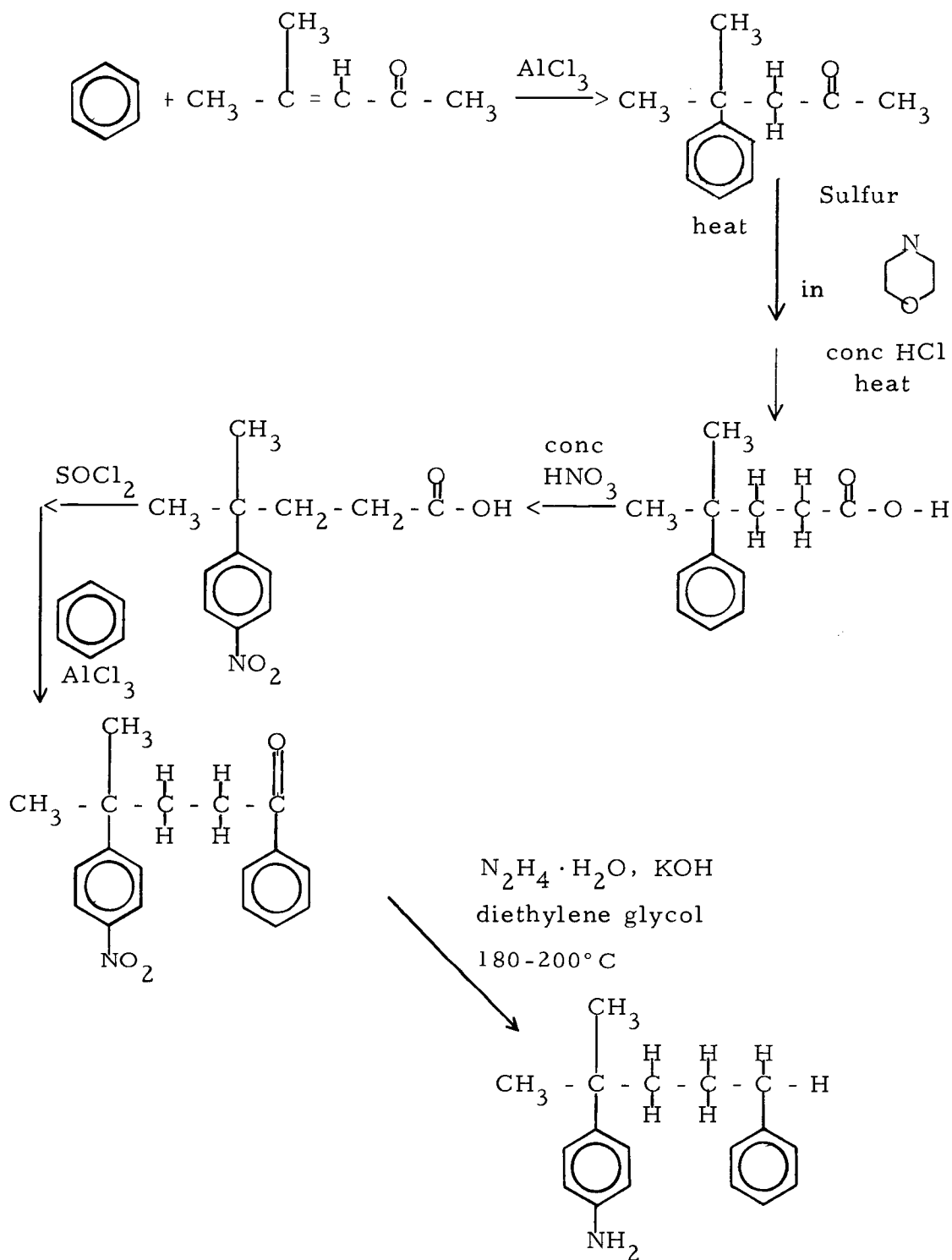
The exceptions to the above scheme were as follows. 1,3-Diphenylpropane was synthesized by a Clemenson reduction of 1,3-diphenyl-2-propanone. 1,4-Diphenylbutane was synthesized by the Wolff-Kishner reduction of the ketone obtained from the reaction of 3-phenylpropyl magnesium bromide with benzonitrile. 1,6-Diphenylhexane was prepared by the direct Wurtz coupling of 1-bromo-3-phenylpropane using sodium metal. 1,2-Diphenylethane was purchased commercially. The α,ω -diphenylalkanes were all 99% pure or greater as shown by gas-liquid chromatographic analysis.

The 1-phenylalkanes were all obtained commercially.

The 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes were synthesized by standard methods. The parent compound, the para-methyl substituted compound, and the ortho- and para-methoxy substituted compounds were prepared by the sequence of reactions in Synthetic Scheme 2. The compounds substituted with bromo, chloro, and nitro were derived from 4-(4-aminophenyl)-4-methyl-1-phenylpentane. The route to this compound is shown in Synthetic Scheme 3. Reaction of the diazonium salt of this compound with hydrochloric acid and cuprous chloride or with hydrobromic acid and cuprous bromide gave respectively the substituted chloro or bromo derivative. These are examples of the use of the Sandmeyer reaction. 4-Methyl-1-(4-nitrophenyl)-1-phenylpentane was made by oxidation of 4-(4-aminophenyl)-4-methyl-1-phenylpentane with peracetic acid. All of the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes were unknown compounds. Physical properties and elemental analyses of these compounds can be found in the experimental part of this thesis. Purification was difficult for many of these compounds. However all except the methyl substituted compound were shown to be at least 97% pure by gas-liquid chromatography before being used. Please see the experimental section of this thesis for further discussion of the methyl substituted compound.



Synthetic Scheme 2. The synthesis of 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes where the substituent is hydrogen, 4-methyl, 2-methoxy or 4-methoxy.



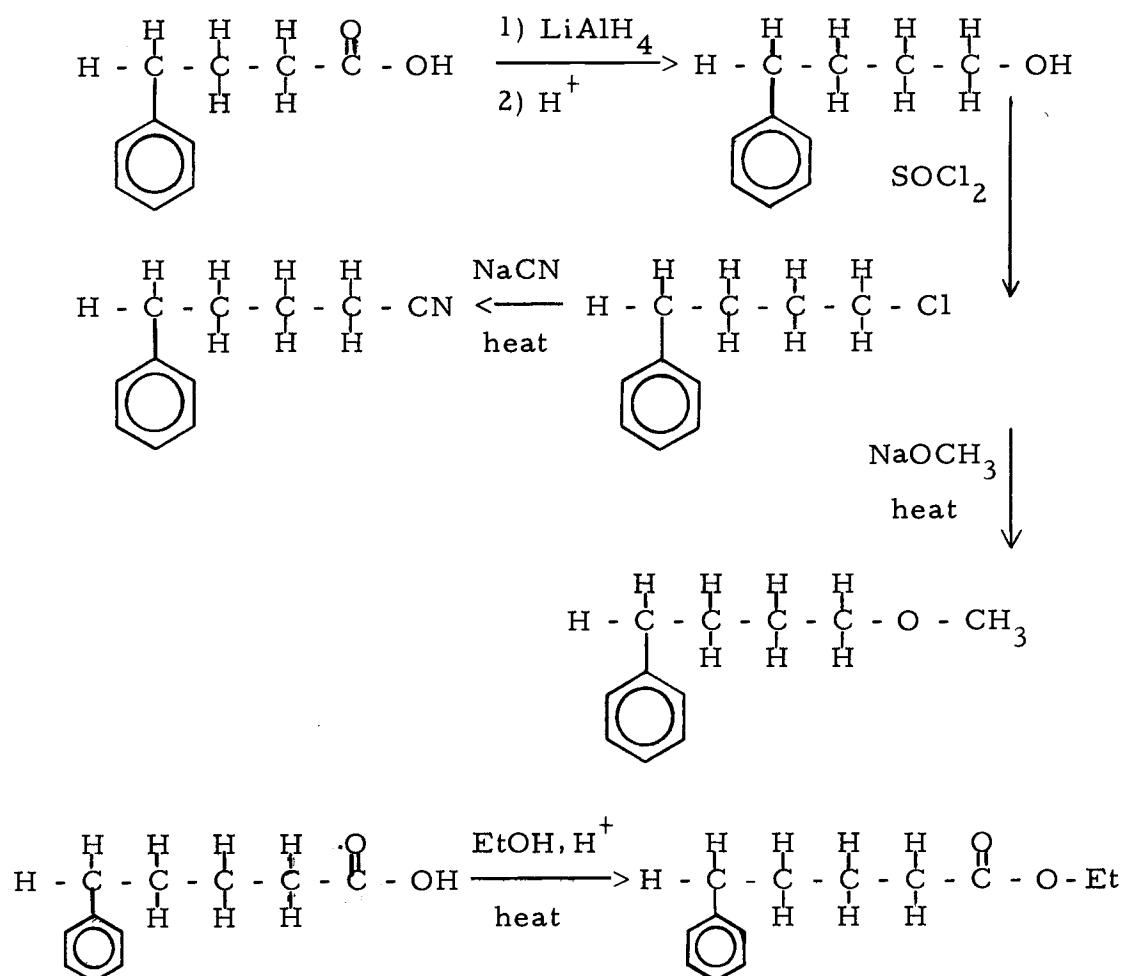
Synthetic Scheme 3. Synthesis of 4-(4-aminophenyl)-4-methyl-1-phenylpentane.

The 4-phenyl-1-substitutedbutane compounds were prepared by methods outlined in Synthetic Scheme 4. 1-Phenylbutane and 1-phenylpentane were obtained commercially. All the compounds in this series were shown to be 98%-100% pure by gas-liquid chromatographic analysis.

Details of the preparation and purification of all the compounds and reagents used in these studies are found in the experimental section of this thesis.

Products of the Reactions

Hydrogen abstraction from α,ω -diphenylalkanes and 1-phenylalkanes by both bromine atom and trichloromethyl radical gave only bromination of the benzylic position. Only benzylic bromination was observed in the reaction of trichloromethyl radical with 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes and with 1-phenyl-4-substitutedbutanes. In the case of the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes no evidence of cyclization after hydrogen abstraction could be observed. A complete discussion of the studies made on the products of hydrogen abstraction from each of the four classes of compounds can be found in the experimental section of this thesis.



Synthetic Scheme 4. Synthesis of 4-phenyl-1-substitutedbutanes.

Relative Rates of Hydrogen Abstraction, Results and Discussion

The goal of the research herein discussed is the evaluation of the importance of a pathway for hydrogen abstraction where the radical is complexed to the substrate, then intramolecularly transferred to the site of hydrogen abstraction. If such a pathway is important the rate of hydrogen abstraction from α, ω -diphenylalkanes

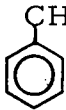
would be expected to be dependent on the length of the carbon chain separating the two ends of the molecule. Since the electronic and the steric environment of the reaction site will also be changed as the end phenyl groups are moved apart some way must be found to estimate these effects.

As an attempt to assess these electronic and steric effects a study of the relative rates of hydrogen abstraction from 1-phenylalkanes was carried out.

The relative rates were obtained by direct competitive techniques at 70°C. Analysis of the samples by gas-liquid chromatography allowed the relative rates of disappearance of the 1-phenylalkanes to be obtained. A complete discussion of the procedures used in these kinetic studies as well as the kinetic expressions used to calculate the relative reactivities can be found in the experimental section of this thesis. The procedures for ascertaining the relative rates of hydrogen abstraction by trichloromethyl radical, generated from bromotrichloromethane, and bromine atom, generated from N-bromo-succinimide were essentially the same. Tables 4 and 5 summarize these results for hydrogen abstraction with trichloromethyl radical and bromine atom respectively.

The relative rate of hydrogen abstraction by both bromine atom and trichloromethyl radical decreased in going from 1-phenylethane to 1-phenylpropane. Addition of one methylene group should increase the

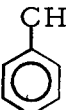
Table 4. Relative rates of benzylic hydrogen abstraction from a series of 1-phenylalkanes by trichloromethyl radical at 70°C. a, b

 $\text{CH}_2-(\text{CH}_2)_n-\text{H}$	No. of Kinetic Runs	$(k_n/k_1)_{\text{H-abst.}}$
n		
1	-	1.00
2	7	0.85 ± 0.04
3	4	0.73 ± 0.05
4	5	0.66 ± 0.04
5	7	0.70 ± 0.04
6	6	0.64 ± 0.01
7	6	0.73 ± 0.01
8	7	0.67 ± 0.01
9	6	0.70 ± 0.04

^aComplete data for each kinetic run are in Appendix 2, Tables 20-27.

^b1-Phenylethane is the reference compound.

Table 5. Relative rates of benzylic hydrogen abstraction from a series of 1-phenylalkanes by the bromine atom at 70°C. a, b

 $\text{CH}_2-(\text{CH}_2)_n-\text{H}$	No. of Kinetic Runs	$(k_n/k_1)_{\text{H-abst.}}$
n		
1	--	1.00
2	9	0.88 ± 0.04
3	6	0.76 ± 0.02
4	5	0.85 ± 0.05
5	12	0.76 ± 0.06
6	5	0.83 ± 0.04
7	10	0.76 ± 0.04
8	7	0.70 ± 0.03
9	10	0.78 ± 0.05

^aComplete data for each kinetic run are in Appendix 1, Tables 12-19

^b1-Phenylethane is the reference compound.

steric hindrance to reaction. A second, less probable cause of decreased reactivity could be that the alpha ethyl group is less able to stabilize the radical than a methyl group is. Ethyl is usually considered more electron donating than methyl but an approach based on hyperconjugation could lead to an opposite conclusion. The correlation of reactivities of α -toluene derivatives with sigma plus parameters supports this latter view (46,66).

Addition of a methylene group to 1-phenylpropane, to give 1-phenylbutane, causes a similar though smaller decrease in reactivity toward both radicals. Further elongation of the side chain produces little change in the relative rates of hydrogen abstraction. For the compounds 1-phenylbutane through 1-phenyldecane nearly constant average relative rates of 0.78 ± 0.03 and 0.70 ± 0.03 are found for bromine atom and trichloromethyl radical respectively. This would suggest that steric and electronic effects of the side chain are nearly constant for these compounds. Both the bromine atom and the trichloromethyl radical show similar selectivities toward reaction with the 1-phenylalkanes. This similarity in selectivity for these radicals of quite different size would imply that simple n-alkyl groups cause little steric hindrance for these reactions.

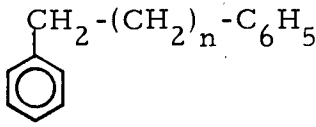
In light of the results discussed above for 1-phenylalkanes, the steric and electronic effects on hydrogen abstraction from α,ω -diphenylalkanes might be predicted. The first compound in the

series, 1,2-diphenylethane, would be expected to be particularly unreactive. The phenyl ring on the carbon next to the site of hydrogen abstraction would be rate retarding both because of its steric hindrance and because of its strong electron withdrawing inductive effect. Introduction of a methylene group between the two benzyl groups of 1,2-diphenylethane, to give 1,3-diphenylpropane, should cause a marked increase in reactivity. Further chain elongation might then cause little change in the observed relative rates.

The results for hydrogen abstraction from α,ω -diphenylalkanes by bromine atom and trichloromethyl radical are shown in Tables 6 and 7 respectively. The same procedures for obtaining the relative rates of reaction were followed for this series of compounds as were employed above for the 1-phenylalkanes.

For the bromine atom there is a marked increase in the rate of reaction in going from 1,2-diphenylethane to 1,3-diphenylpropane. A similar though smaller effect is observed for addition of a second methylene group between the two benzyl groups. These results are as predicted from steric and electronic effects of the second phenyl group near the reaction site. A nearly constant relative rate of hydrogen abstraction of 1.48 ± 0.09 is observed for the compounds 1,3-diphenylpropane through 1,10-diphenyldecane. These results suggest that changes in reactivity observed with chain elongation can be explained by steric and electronic effects. There is thus no

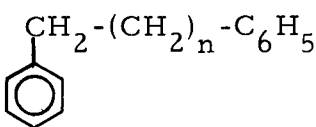
Table 6. Relative rates of benzylic hydrogen abstraction from a series of α,ω -diphenylalkanes by bromine atom at 70°C. a, b

	No. of Kinetic Runs	$(k_n/k_1)_{\text{H-abst.}}$
n		
1	--	1.00
2	6	1.48 ± 0.06
3	12	1.64 ± 0.08
4	11	1.35 ± 0.07
5	9	1.55 ± 0.08
6	11	1.46 ± 0.09
7	10	1.35 ± 0.13
8	10	1.35 ± 0.08
9	7	1.61 ± 0.06

^a Complete data for each kinetic run are in Appendix 3, Tables 28-35.

^b 1,2-Diphenylethane is the reference compound.

Table 7. Relative rates of benzylic hydrogen abstraction from a series of α,ω -diphenylalkanes by trichloromethyl radicals at 70°C. a, b

	No. of Kinetic Runs	$(k_n/k_1)_{\text{H-abst.}}$
n		
1	--	1.00
2	4	2.01 ± 0.11
3	5	2.42 ± 0.15
4	22	2.51 ± 0.25
5	12	3.17 ± 0.22
6	7	2.90 ± 0.09
7	7	2.60 ± 0.14
8	7	2.18 ± 0.11
9	6	2.40 ± 0.12

^a Complete data for each kinetic run are in Appendix 4, Tables 36-43.

^b 1,2-Diphenylethane is the reference compound.

evidence for a large effect due to intramolecular transfer to the site of hydrogen abstraction.

The results for hydrogen abstraction by the trichloromethyl radical from α,ω -diphenylalkanes are much different than those obtained with bromine atom. There is a much larger dependence of the relative rates on changes in chain length. The rate of hydrogen abstraction doubled in going from 1,2-diphenylethane to 1,3-diphenylpropane. Since trichloromethyl radical and bromine atom are similarly influenced by inductive effects, this greater dependence on chain length is probably due to steric factors. In reaction with 1,2-diphenylethane the unfavorable non-bonding interactions between the phenyl group and the large trichloromethyl radical would be expected to be particularly severe. A second and more interesting difference between the trichloromethyl radical results and those of the bromine atom is that no constant relative rate of hydrogen abstraction by the trichloromethyl radical is observed for the compounds 1,4-diphenylbutane through 1,10-diphenyldecane. This difference is illustrated in Figure 7. The relative rate of reaction increases steadily from 1,2-diphenylethane through 1,6-diphenylhexane then decreases from 1,7-diphenylheptane through 1,9-diphenylnonane.

This difference in the dependence of rate on chain elongation for trichloromethyl radical would not seem to arise from steric or

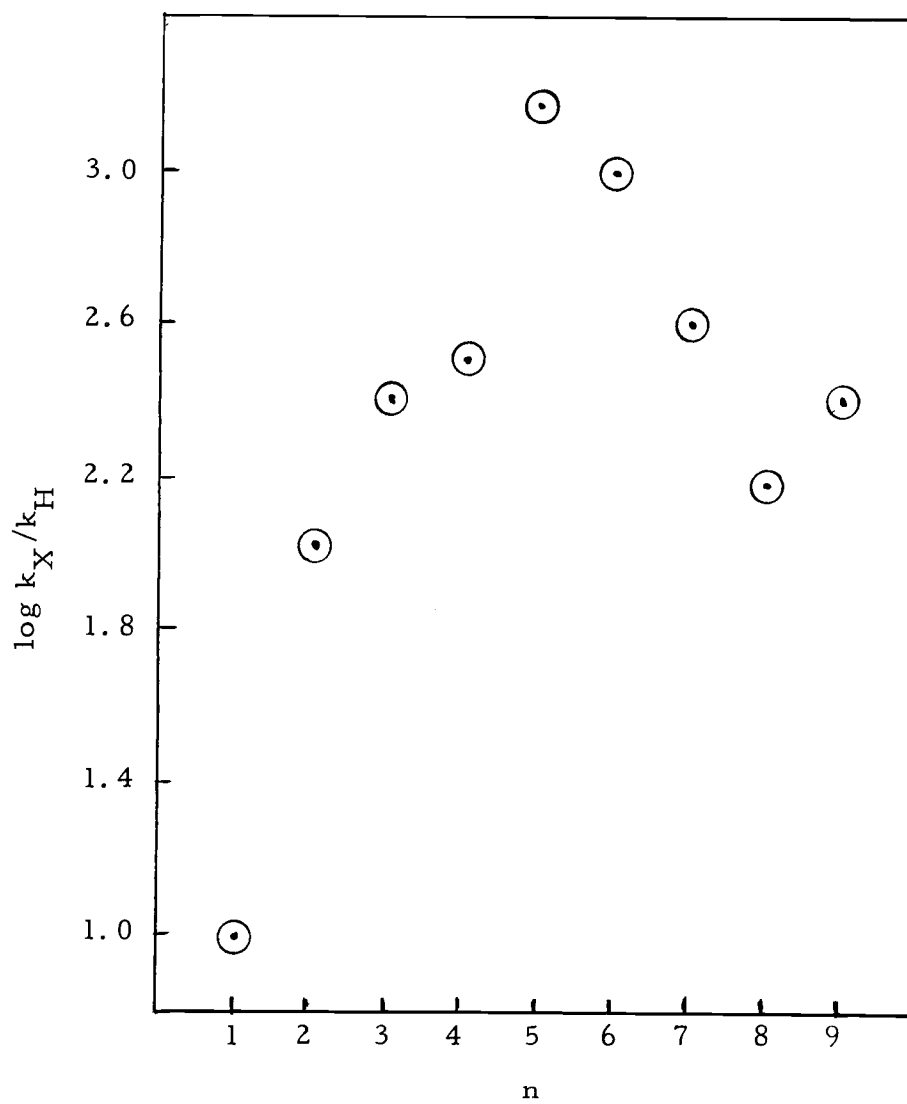


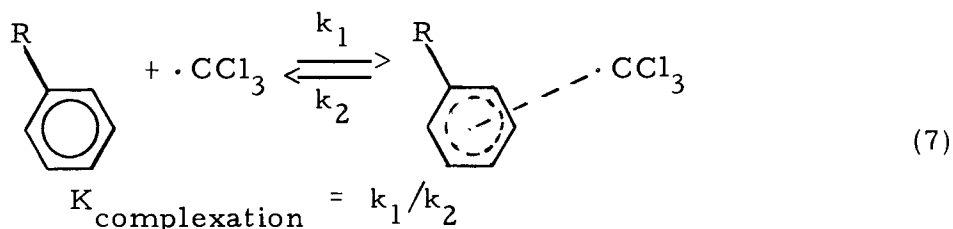
Figure 7. The relative rates of hydrogen atom abstraction by $\cdot\text{CCl}_3$ from $\text{C}_6\text{H}_5\text{-CH}_2(\text{CH}_2)_n\text{-C}_6\text{H}_5$ versus n .

electronic effects. The results with bromine atom suggest that these effects are nearly constant after about 1,3-diphenylpropane. The rate maximum observed for 1,6-diphenylhexane is not due to experimental uncertainty. The average of the relative rates of the compounds 1,3-diphenylpropane through 1,10-diphenyldecane was 2.52 ± 0.27 . The relative rate for 1,6-diphenylhexane of 3.17 ± 0.22 is well above this average and outside its range of uncertainty. An attractive explanation for these results is that the trichloromethyl radical is first complexed to the phenyl ring of one end of the substrate and then intramolecularly transferred to the opposite end of the molecule where hydrogen abstraction takes place.

If such a pathway of radical complexation and intramolecular transfer is operative, then the observed relative rates of hydrogen abstraction will be dependent on the relative rates of three different processes. This dependence is summarized in Equation 6.

$$\begin{aligned}
 k_{\text{observed relative}} &= \frac{K_{\text{A complexation}}}{K_{\text{B complexation}}} \times \frac{k_{\text{A transfer}}}{k_{\text{B transfer}}} \\
 \text{rate of A to B} & \\
 & \times \frac{k_{\text{A hydrogen abstraction}}}{k_{\text{B hydrogen abstraction}}}
 \end{aligned}
 \tag{6}$$

$K_{\text{complexation}}$ is the equilibrium constant for the complexation of the radical as shown in Equation 7.



The value of $K_{\text{complexation}}$ should be about constant for the compounds in the series 1,4-diphenylbutane through 1,10-diphenyldecane since the electron density of the aromatic rings in all these compounds should be approximately equal. The rate of hydrogen abstraction, $k_{\text{hydrogen abstraction}}$, by the transferred trichloromethyl radical for all the α,ω -diphenylalkanes should also be equal. Both electronic and steric effects should be constant for the members of this series with from four to ten methylene units between the phenyl groups.

The rate of transfer of the complexed radical, k_{transfer} , should be dependent on the length of the alkyl chain connecting the two phenyl groups. The ease of transfer will depend upon the number of conformations of the molecule that can favorably bring its two ends together. This dependence on conformation will in turn be dependent upon the chain length. Thus the dependence we see between the relative rate of hydrogen abstraction and chain length is what is expected for a process where a radical is first complexed then intramolecularly transferred to a site of hydrogen abstraction.

Hydrogen abstraction from these compounds can take place by

two other pathways besides the one discussed above. First, some reaction will take place by uncomplexed trichloromethyl radicals. The total concentration of aromatic moieties in these studies should be such that this type of reaction should have little effect upon the observed relative rates. The second path for reaction is for intermolecular transfer of the trichloromethyl radical to a reactive site on a molecule other than the one it is complexed to. The extent of this type of radical reaction should also be concentration dependent. Since concentration was kept reasonably constant in these studies, intermolecular transfer and reaction should cause little effect upon the relative rates of hydrogen abstraction as chain length is changed.

Equation 6 above suggests a second way to observe the effects of complexation upon hydrogen abstraction. A series of compounds where the distance between the site of complexation and the site of abstraction is held constant should show a constant rate of radical transfer. If the electronic and steric environment at the site of hydrogen abstraction is held constant for this same series of compounds then the rate of hydrogen abstraction should also be constant. On the other hand, if electron density at the site of complexation is varied, then the equilibrium constant for complexation should change. The electron density of an aromatic compound can easily be changed by adding electron donating or electron withdrawing substituents. Thus any observed dependence of the relative rates of hydrogen

abstraction in this series of compounds upon changes in substituents should parallel the extent of complexation. The compound that complexes the most trichloromethyl radicals should react the fastest.

The 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes should meet the requirements outlined above. The distance between site of complexation, the substituted phenyl, and the opposite benzylic position is fixed. Reaction can only take place at the benzylic position opposite the site of complexation since the other benzylic position is bonded to two methyl groups. The three methylene groups between the reaction site and the substituted phenyl group should insulate the reaction site from the inductive effects of the substituted phenyl group. Thus, the reaction site of this class of compounds should have a nearly constant electronic and steric environment.

The results from hydrogen abstraction from the α,ω -diphenylalkanes suggest that a system where the site of hydrogen abstraction is three carbons away from the complexing aromatic ring may not be optimum to observe intramolecular radical transfer. The reasons this system was chosen are experimental in nature. When work was begun on this problem, this series appeared to be relatively easy to synthesize. Also this system had the lowest molecular weight where complexation and transfer might be expected. It was initially planned to obtain the relative rates of hydrogen abstraction by analysis with gas-liquid chromatography. Analysis of compounds of high molecular

weight necessitates high operating temperatures and hence a greater possibility of decomposition of the bromide product of the reaction. Since product decomposition can interfere with analysis, the compounds with the lowest possible molecular weights were used.

Table 8 summarizes the results of hydrogen abstraction by trichloromethyl radical from 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes. The relative rates were obtained by direct competition techniques at 70°C. Analysis of the samples by nuclear magnetic resonance spectroscopy allowed the relative rates of disappearance to be obtained. Complete details of these experiments can be found in the experimental section of this thesis.

Table 8. Relative rates of hydrogen abstraction from a series of 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes by trichloromethyl radical at 70°C. ^{a, b}

Substituent	σ	σ^+	No. of Kinetic Runs	$(k_X/k_H)_{H-abst}$
p-CH ₃ O	-0.268	-0.778	5	1.25 ± 0.03
p-CH ₃	-0.170	-0.311	5	1.06 ± 0.04
H	0.000	0.000	12	1.04 ± 0.04
p-Cl	+0.227	+0.114	7	0.66 ± 0.03
p-NO ₂	+0.778	+0.790	6	0.48 ± 0.02
p-Br ^c	+0.232	+0.150	13	1.09 ± 0.10
o-CH ₃ O ^c			6	1.50 ± 0.03

^aComplete data for each kinetic run are in Appendix 5, Tables 44-50.

^bDiphenylmethane is the reference compound.

^cNot used in the calculation of rho from the Hammett equation.

The logarithms of the relative rates of reaction correlate with sigma of a given substituent in the Hammett equation to give a rho value of -0.40. A correlation coefficient of -0.971 is obtained. Figure 8 shows a plot of the logarithms of the relative rates versus sigma for these compounds. The point representing the relative rate of 4-(4-bromophenyl)-4-methyl-1-phenylpentane lies far off the best line. The results for this compound were not used in the calculation of rho. The relative rate of hydrogen abstraction for 4-(2-methoxyphenyl)-4-methyl-1-phenyl pentane was also not used in the calculation of rho. In this compound there is the possibility of some type of steric effect from the ortho-substituent. The observed relative rate, however, is about what would be expected for a compound with a substituent parameter of -0.33 or -0.39. These values of the ortho substituent constant for methoxy were obtained from the detritiation of phenylacetylenes (67) or the acid and base hydrolysis of ethyl benzoates (68, 31).

A rho value of -0.40 suggests a significant long range electronic effect upon this hydrogen abstraction reaction. This rho value could be a measure of the inductive effect of the substituted phenyl group upon the reaction site. As discussed above this is an unlikely explanation since the reaction site and the substituted phenyl group are separated by three methylene groups. These methylene groups should effectively insulate the reaction site.

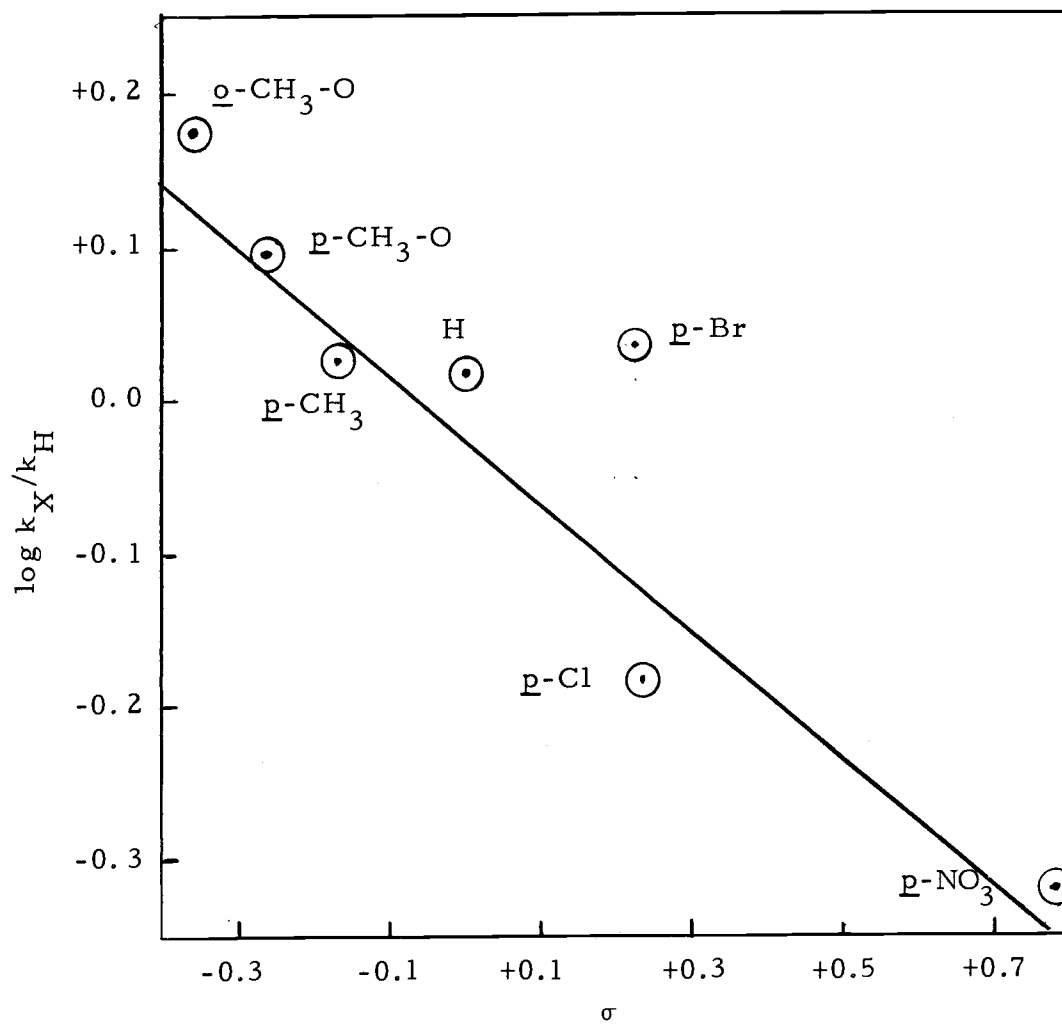


Figure 8. The relative rates of hydrogen atom abstraction by $\cdot\text{CCl}_3$ from 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes versus σ .

$\rho = -0.40$ (excluding o-OCH_3 and p-Br)

Corr. coef. = -0.971

In an effort to evaluate possible long range inductive effects upon hydrogen abstraction reactions, the relative rates of hydrogen abstraction by trichloromethyl radical from a series of 4-phenyl-1-substitutedbutanes were obtained. The results are summarized in Table 9. The relative rates were obtained by direct competition techniques at 70°C. Analysis of the samples by nuclear magnetic resonance spectroscopy allowed the relative rates of disappearance to be obtained. All reaction was observed to take place at the benzylic position. Complete details of these kinetic studies can be found in the experimental section of this thesis.

Table 9. Relative rates of hydrogen abstraction from a series of 1-phenyl-4-substitutedbutanes by trichloromethyl radical at 70°C. a, b

Substituent	σ^*	No. of Kinetic Runs	$(k_X/k_H)_{H-abst.}$
CH ₂ -CH ₃	-0.10	6	1.11 ± 0.04
CH ₂ -H	0.00	5	1.07 ± 0.04
CH ₂ -O-CH ₃ O	+0.64	6	0.87 ± 0.03
CH ₂ -C-O-Et	+0.71	7	0.55 ± 0.02
CH ₂ -Cl	+1.05	6	0.57 ± 0.03
CH ₂ -CN	+1.30	6	0.37 ± 0.04

^a Complete data for each kinetic run are in Appendix 6, Tables 51-58.

^b Diphenylmethane is the reference compound.

The logarithms of the relative rates of hydrogen abstraction by trichloromethyl radical from 4-phenyl-1-substitutedbutanes could be correlated with the Taft polar substituent constants, also called sigma star constants, to give a rho of -0.32 with a correlation coefficient of 0.935. This correlation is illustrated in Figure 9. This negative rho value would indicate a large buildup of positive charge in the transition state of the hydrogen abstraction. The substituents in this series of compounds are insulated by three methylene groups from the site of reaction yet they still have a significant influence upon the rate of reaction.

The dependence of the relative rates of hydrogen abstraction upon substituent observed in the 4-methyl-1-phenyl-4-(substituted-phenyl)pentane series might also arise from a long range inductive effect. If this is so, then the logarithms of the relative rates of hydrogen abstraction from these compounds should correlate with the respective sigma star constants for the substituted phenyl ring. This correlation should give a rho value similar to that obtained above with the 1-phenyl-4-substitutedbutanes.

In order to maintain consistency with the 1-phenyl-4-substituted-butane results, the substituents in the 4-methyl-1-phenyl-4-(substitutedphenyl)pentane series will be taken to be the substituted benzyl group consisting of carbon 4 and the substituted phenyl ring. The sigma star values of substituted benzyl groups have been

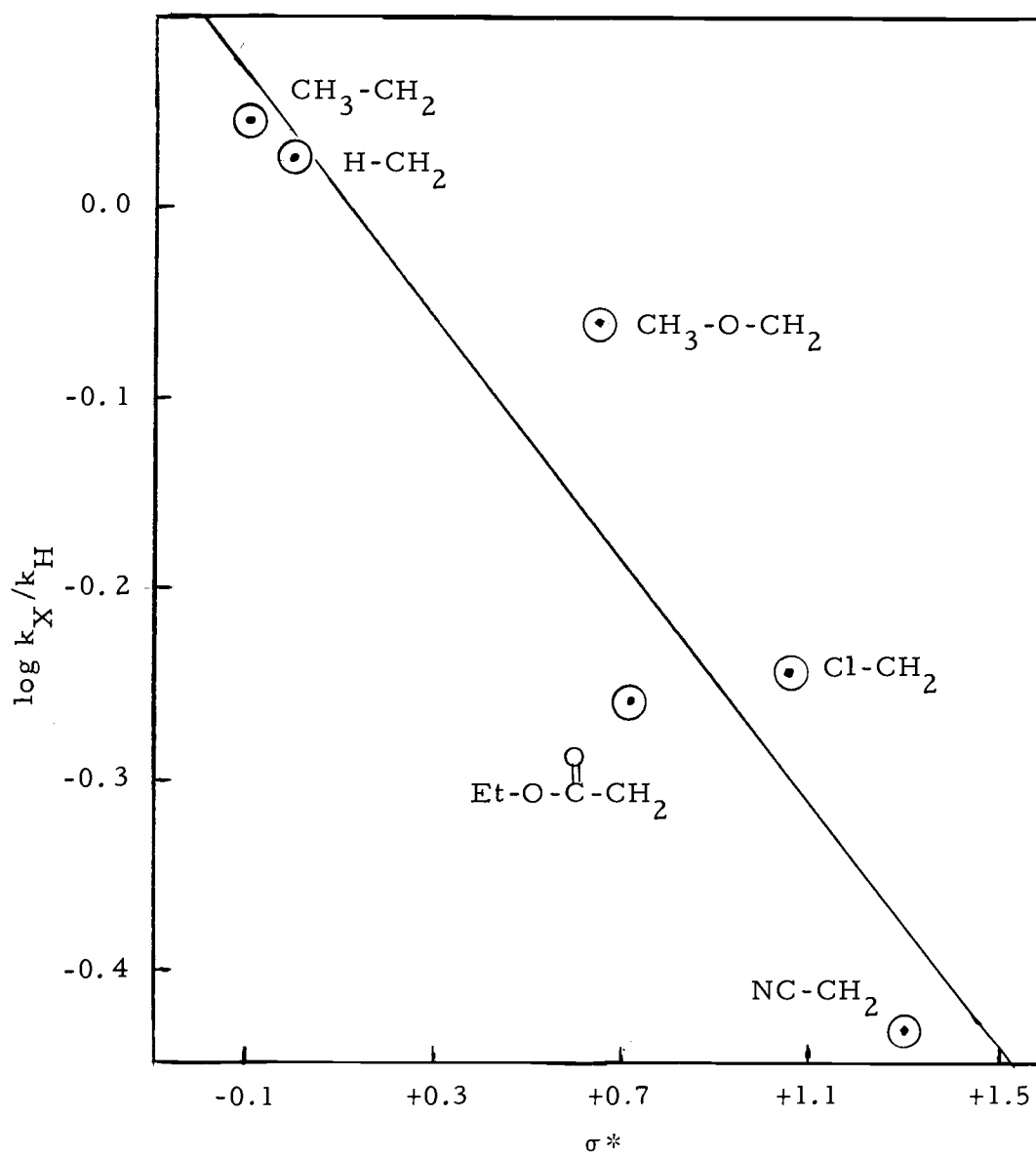


Figure 9. The relative rates of hydrogen atom abstraction by $\cdot\text{CCl}_3$ from 4-phenyl-1-substitutedbutanes versus σ^* .

$$\rho = -0.32$$

$$\text{Corr. coef.} = -0.935$$

calculated in at least two different ways. First, they have been estimated from ionization constant data from the corresponding arylacetic acids (69). In a second method, the Taft polar substituent constants have been calculated from ^{29}Si -H coupling constants for a series of substituted phenylsilanes, phenylmethylsilanes and phenyldimethylsilanes. This method gives the sigma star values for substituted phenyl groups (70). Division by 2.8, the fall off factor per methylene group suggested by Taft (31), should give the corresponding substitutedbenzyl sigma star constants (70). The sigma star values obtained from each of the methods above were found to correlate with the pK_a values (71) of substituted β -arylisovaleric acids (Figure 10) obtained at 25°C in 50% water-ethanol mixtures. Sigma star constants obtained by the first method above gave a rho value of -1.35 with a correlation coefficient of -0.996. The sigma star constants obtained by the second method above gave a rho value of -1.49 with a correlation coefficient of -0.969.

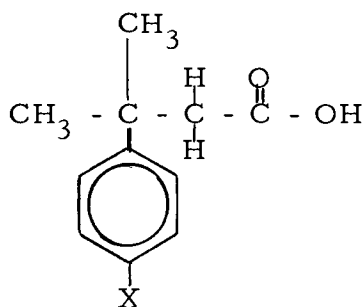


Figure 10. Substituted β -arylisovaleric acids.

The logarithms of the relative rates of hydrogen abstraction by trichloromethyl radicals from the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes can be correlated with sigma star constants obtained by either method discussed above. The relative rates and the corresponding sigma star values for each compound are shown in Table 10. A rho of -1.34 with a correlation coefficient of -0.960 is obtained with the sigma star constants calculated from the ionization constants of arylacetic acids. Correlation with sigma star constants obtained from ^{29}Si -H coupling constants gave a rho value of -1.54 with a correlation coefficient of -0.975.

A complete study of polar substituent effects upon the relative rates of hydrogen abstraction should also include the effects of the two methyl groups bonded to the same carbon as the substitutedphenyl group. Since these are electron donating groups they should stabilize the transition state for hydrogen abstraction. This stabilization should decrease the dependence of the relative rates upon phenyl substituents thus decreasing the absolute value of rho. Using this line of reasoning, the absolute value of rho for a system such as 1-phenyl-4-(substitutedphenyl)butanes, which does not possess these methyl groups, should be larger than the rho found for the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes. In reality the effects of these two methyl groups are probably very small and could be disregarded. That, indeed, the effects of these methyl groups are unimportant is

Table 10. Relative rates of hydrogen abstraction from a series of 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes by trichloromethyl radical at 70°C. a, b

Substituent	σ^* Method I ^d	σ^* Method II ^e	No. of Kinetic Runs	$(k_X/k_H)_{H-abst}$
p-CH ₃ O	0.215	0.129	5	1.25 ± 0.03
p-CH ₃	0.220	0.164	5	1.06 ± 0.04
H	0.250	0.207	12	1.04 ± 0.04
p-Cl	0.330	0.268	7	0.66 ± 0.03
p-NO ₂	0.510	0.407	6	0.48 ± 0.02
p-Br ^c	---	0.26	13	1.09 ± 0.10
o-CH ₃ O ^c	---	0.15 ^f	6	1.50 ± 0.03

^a Complete data for each kinetic run are in Appendix 5, Tables 44-50.

^b Diphenylmethane is the reference compound.

^c Not used in the calculation of rho from the Taft equation.

^d σ^* calculated from ionization constants of arylacetic acids (69)

^e σ^* calculated from ²⁹Si-H coupling constants (70).

^f σ^* calculated from ionization constant of o-methoxy-β-phenyl propionic acid. Adjusted to fit with values from method II.

suggested by a comparison of the rho values obtained when the pK_A values of substituted arylisovaleric acids and substituted arylpropanoic acids are correlated with sigma in the Hammett equation (71). The two methyl groups, being electron donating, should destabilize the carboxylate anion in the substituted arylisovaleric acid series and thus increase the absolute value of rho. In reality the two rho values are the same within experimental error (71).

The absolute value of rho, -1.34 or -1.54, obtained by correlation of the logarithms of the relative rates for hydrogen abstraction by trichloromethyl radicals from the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes with sigma star are nearly five times larger than the rho, -0.32, obtained for the corresponding reaction with the 4-phenyl-1-substitutedbutanes. Graphic representations showing the logarithms of the relative rates versus sigma star for both sets of compounds are shown in Figures 11 and 12. This large difference in rho values would suggest that the cause of substituent dependence is different for these two sets of compounds. The large long range substituent effect observed for the 4-methyl-1-phenyl-4-(substitutedphenyl)pentane series thus probably arises mostly from some factor other than simple inductive effects.

The logarithms of the relative rates of hydrogen abstraction by trichloromethyl radical from the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes can also be made to correlate with sigma plus

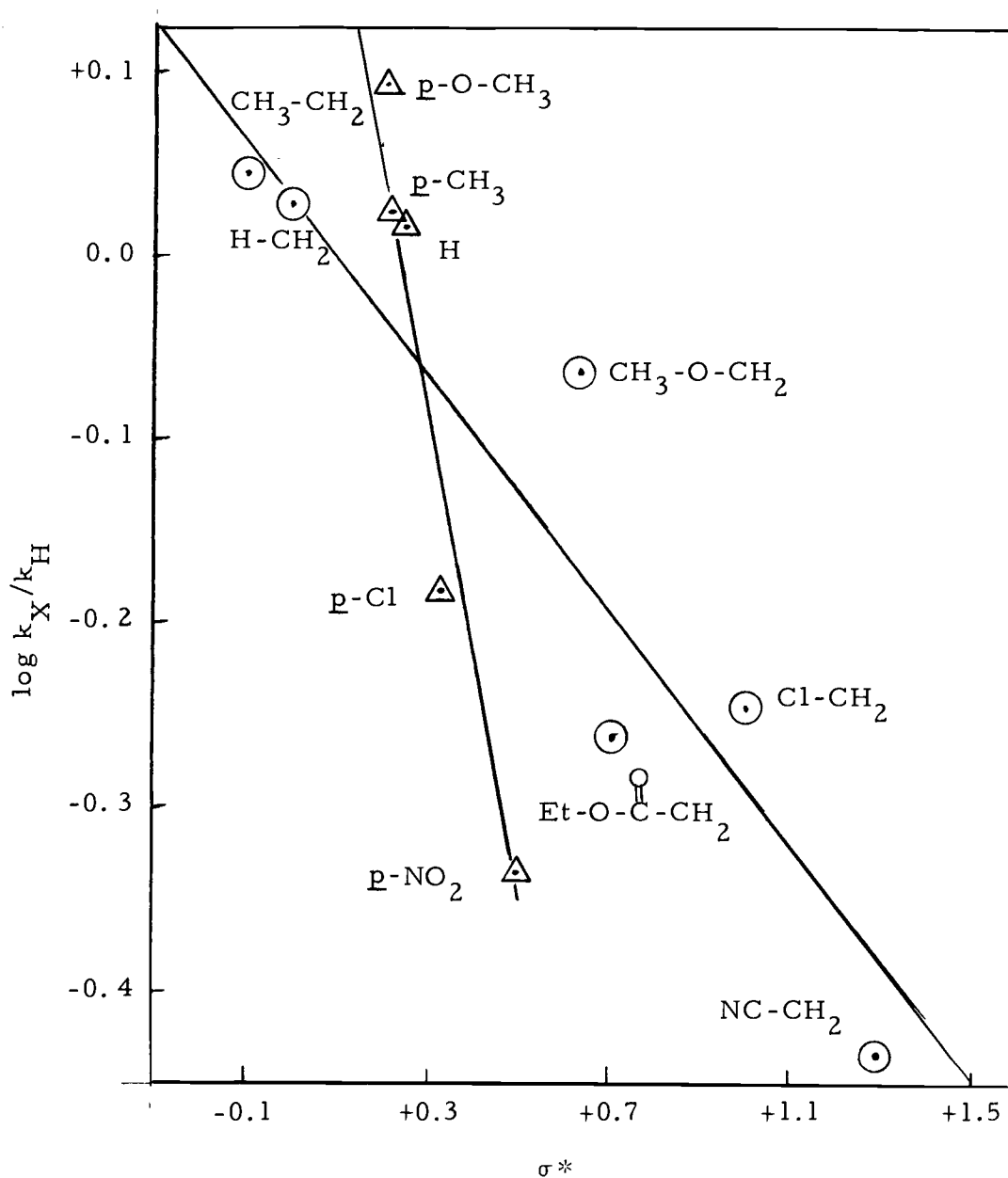


Figure 11. The relative rates of hydrogen atom abstraction by $\cdot\text{CCl}_3$ from 4-phenyl-1-substitutedbutanes, \odot , and 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes,^(a) \triangle .

(a) σ^* calculated from phenylacetic acid ionization constants giving $\rho = -1.34$ with corr. coef. = -0.960 .

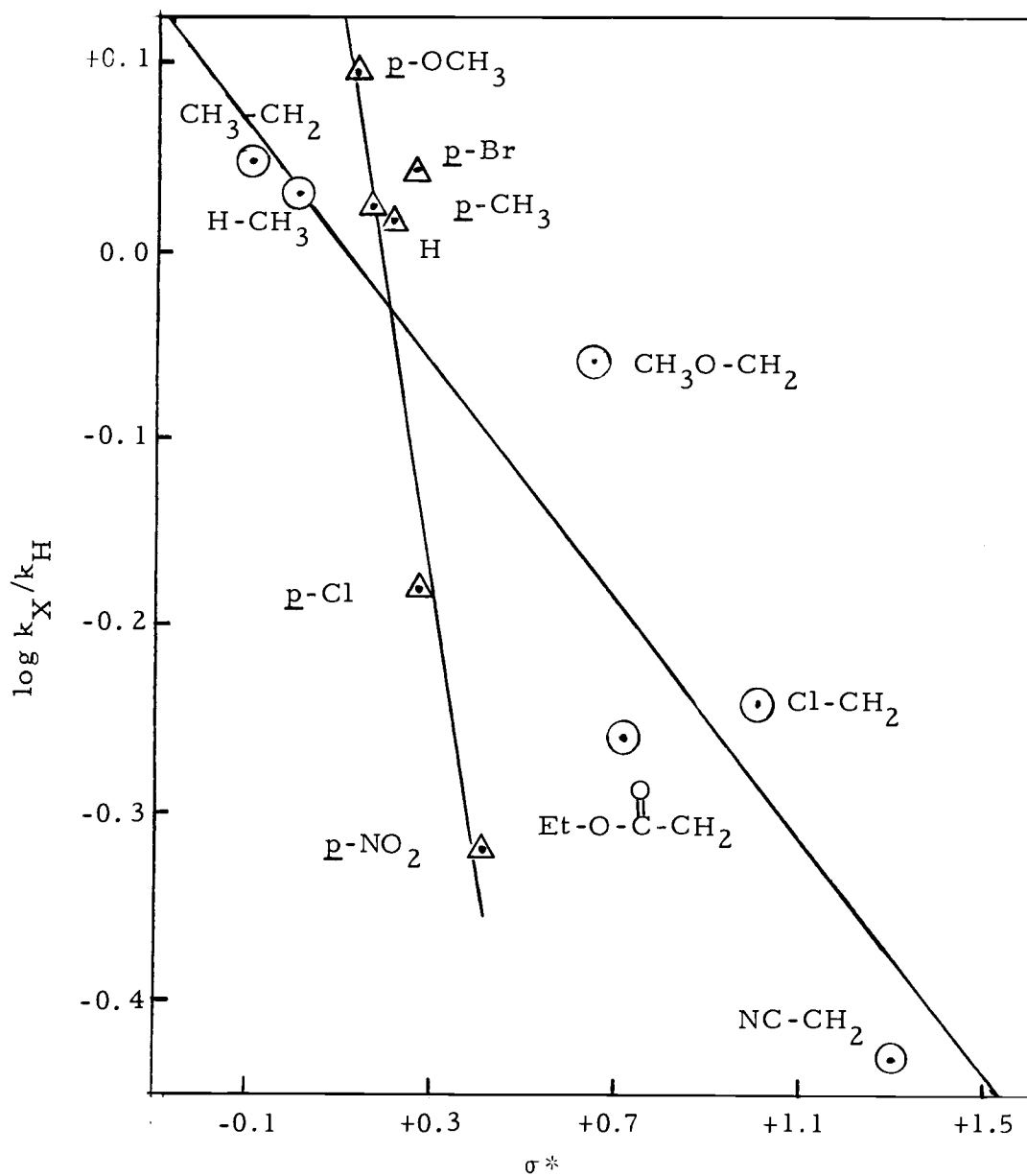


Figure 12. The relative rates of hydrogen atom abstraction by $\cdot\text{CCl}_3$ from 4-phenyl-1-substitutedbutanes, \odot , and 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes, \triangle .

(a) σ^* calculated from ^{29}Si -H coupling constants giving $\rho = -1.54$ with corr. coef. = -0.975 (excluding p-Br).

constants to give a rho of -0.28 with a correlation coefficient of -0.928. Figure 13 shows a plot of the logarithms of the relative rates versus sigma plus for these compounds. The point representing the relative rate of reaction of the bromo substituted compound again lies far off the best line. The results for this compound were not used in the calculation of rho. Once again the rho value indicates a large substituent effect upon the relative rates.

The rho values obtained by correlating the logarithms of the relative rates of hydrogen abstraction from the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes with sigma and sigma plus in the Hammett equation and with sigma star in the Taft equation suggest a large substituent effect upon the rate of hydrogen abstraction. Comparison with the results from the 1-phenyl-4-substitutedbutane series suggests that this large long range substituent dependence is not a simple inductive effect. The substituent dependence observed can be explained if it is assumed that it reflects effects of complexation on the rate of hydrogen abstraction. The compounds with electron donating substrates complex the most radicals. If the rate of intramolecular transfer and the rate of hydrogen abstraction by transferred trichloromethyl radicals is nearly constant for the whole series of compounds; then the differences in relative rates observed mirror the difference in the number of trichloromethyl radicals complexed. The compounds that complex the most radicals react the fastest.

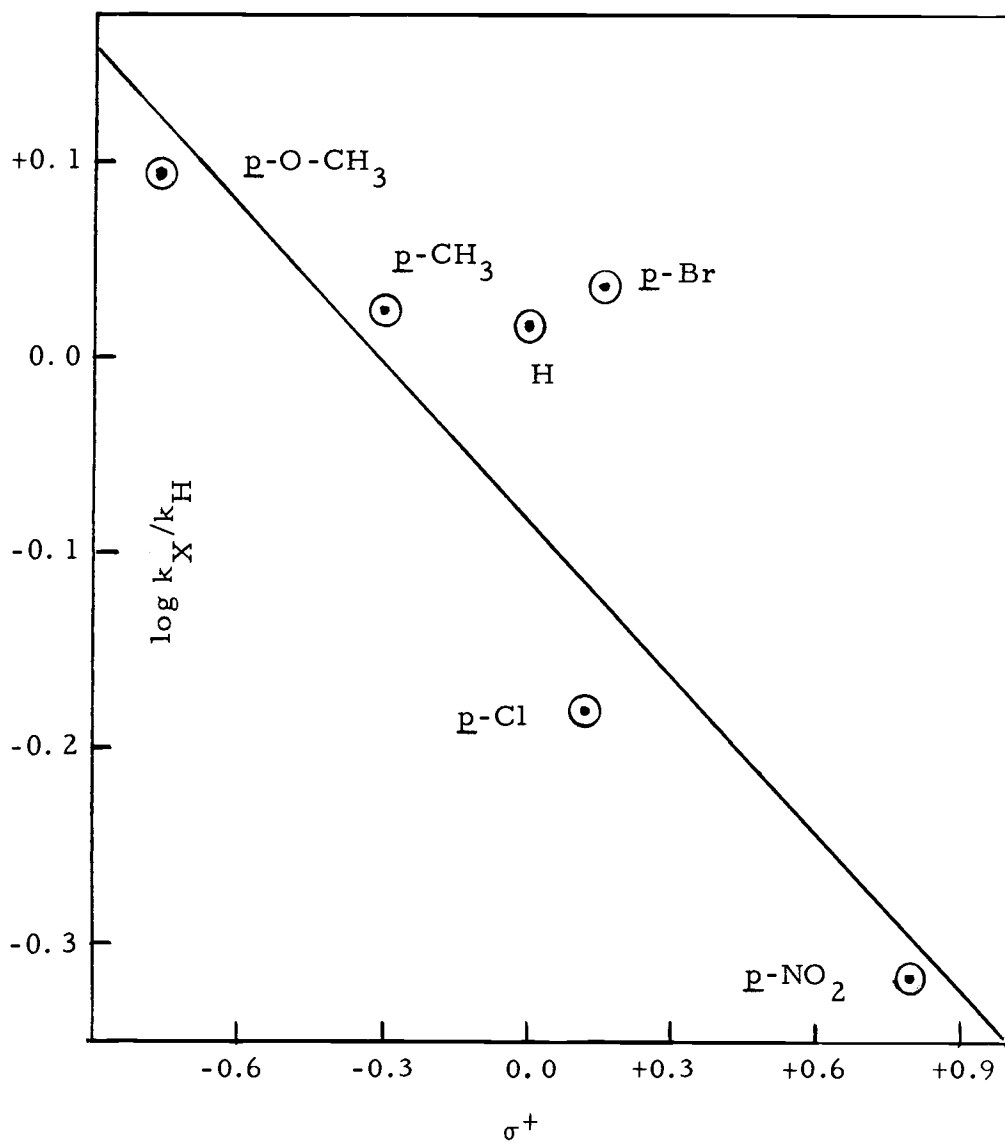


Figure 13. The relative rates of hydrogen atom abstraction by $\cdot\text{CCl}_3$ from 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes versus σ^+ .

$$\rho = -0.28$$

$$\text{Corr. coef.} = -0.928$$

The fact that a better correlation of the results is found with σ rather than σ^+ may also be evidence for a complexed radical phenomenon. The results of Russell (48) concerning changes in radical selectivity with changes in solvent and the results of Martin and Gleicher (54) concerning radical additions to 4-substituted-phenyl-1-butenes are explained by assuming radical complexation before reaction. Both sets of data correlate best with σ constants in the Hammett equation.

It is of interest to compare the relative rates of hydrogen abstraction by trichloromethyl radical from 1,4-diphenylbutane and 4-methyl-1,4-diphenylpentane. On a per benzylic hydrogen basis the latter compound is 2.7 times more reactive than the former. From an inductive model the extra electron donating effect from these methyl groups might make the 4-methyl-1,4-diphenylpentane 1.2 times more reactive than 1,4-diphenylbutane. However there is a second way these two methyl groups may increase reactivity. They may donate electron density into the phenyl ring next to them. An increase in electron density would promote complexation. If a significant amount of reaction is by trichloromethyl radicals that are first internally complexed to the aromatic ring and then intramolecularly transferred to the site of reaction the more complexation should mean a greater relative rate of reaction for the 4-methyl-1,4-diphenylpentane. Russell found that the relative reactivity of tertiary to

primary hydrogens in 2,3 dimethylbutane went from 16.3 in 4 M. ethylbenzene to 24 in 4 M tert-butylbenzene. This was explained by assuming more complexation in the latter solvent than the former (48). The two compounds compared in this discussion should approximate these two substituted benzenes in ability to form pi complexes.

As discussed in the introduction of this thesis, a pi or charge transfer complex can be represented as a resonance hybrid of a "no-bond" structure held together by weak electrostatic interactions and a charge-transfer structure where an electron has been transferred from the donor to the acceptor. Here a strong electrostatic interaction between a full positive and full negative charge would hold the complex together. If the charge-transfer structure makes an important contribution to bonding in the complex then the stability of the complex and thus the magnitude of its equilibrium constant should be a function of the ionization potential of the donor. It might be expected that the logarithms of the relative rates of hydrogen abstraction by trichloromethyl radical from 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes would correlate with the ionization potentials of the substituted phenyl portion of the molecule. A plot of these logarithms versus the ionization potentials of substituted benzenes (72) is shown in Figure 14. The slope of this line is -0.24 and the correlation coefficient is only -0.829. A very poor correlation is obtained. This would suggest that the pi complexes involved in these hydrogen

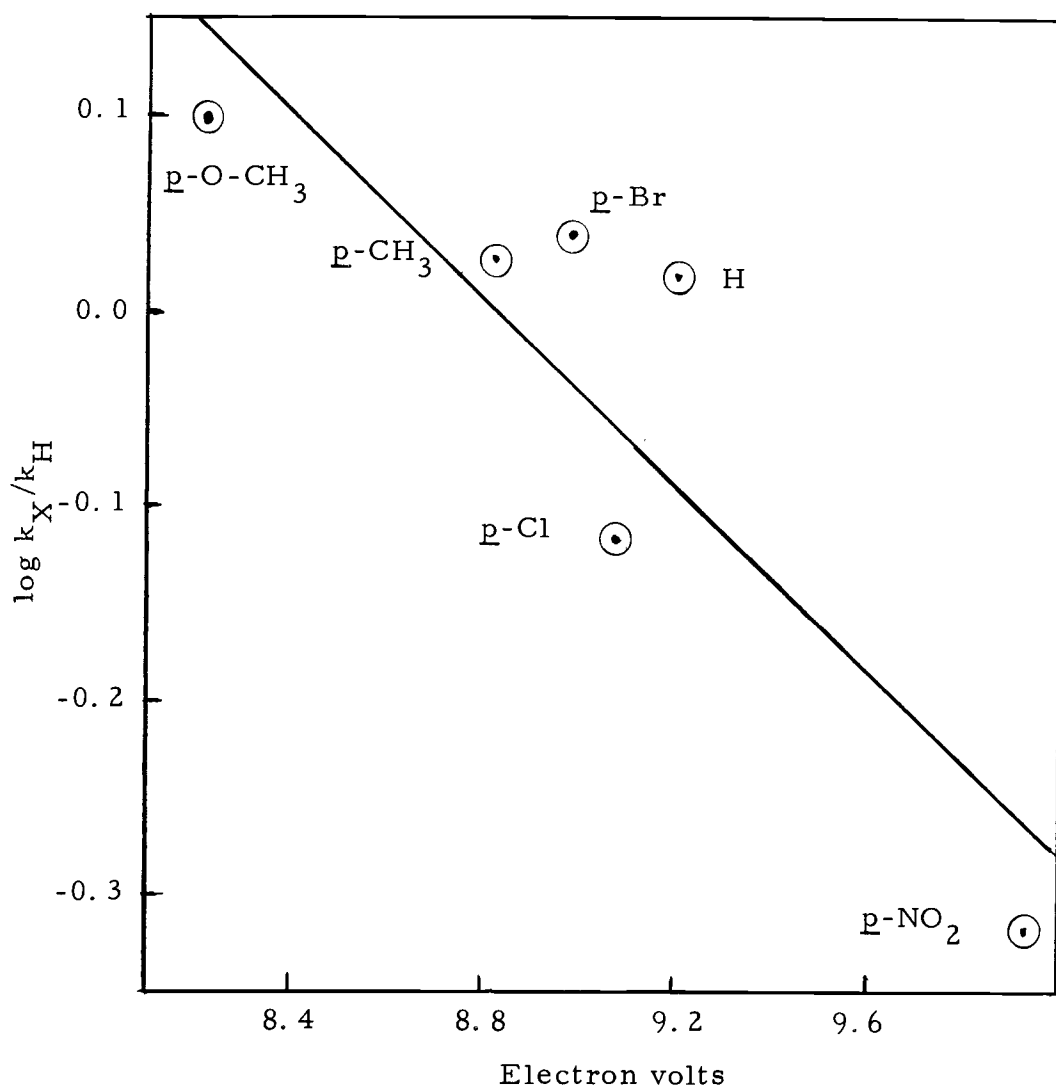


Figure 14. The relative rates of hydrogen atom abstraction by $\cdot\text{CCl}_3$ from 4-methyl-1-phenyl-4-(substitutedphenyl)-pentanes versus ionization potentials.

$$\rho = -0.24$$

$$\text{Corr. coef.} = -0.829$$

abstraction reactions have important contributions from the "no-bond" structure. The electrostatic interaction in this type of structure should be dependent upon the overall electron density of the aromatic ring and should correlate with the sigma constant of the substituted phenyl ring. Thus a correlation between the logarithms of the relative rate of hydrogen abstraction involving pi complexation and sigma constants is expected and is observed.

The results for 4-(4-bromophenyl)-4-methyl-1-phenylpentane do not correlate with sigma or sigma plus. This compound is much more reactive than would be expected and its reactivity does in some degree parallel its ionization potential. Perhaps the trichloromethyl radical can complex with the bromine substituent itself and then be intramolecularly transferred to the site of hydrogen abstraction. This type of halogen-radical complex was suggested to explain the high tertiary to primary product ratio of 3:1 observed for the chlorination of 2,3-dimethylbutane in 4 M iodobenzene (48). Some experimental effect may also be responsible for the anomalous results for the bromine substituted compound. The relative rate observed for this compound had an uncertainty nearly double that of any of the other compounds of this series.

So far the substituent effect observed in hydrogen abstraction from the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes has been explained as arising from the difference in the extent of complexing

between the trichloromethyl radical and the substituted phenyl end of the substrate. A second type of complexation effect is possible. The benzylic radical formed as trichloromethyl radical abstracts hydrogen might be complexed by the substituted phenyl ring at the opposite end of the molecule. An anchimeric assistance can be envisioned if the complex is being formed as the hydrogen is being removed. This complexation effect would also be dependent upon the electron density of the substituted aromatic ring. Thus long range substituent effects such as were observed in these results would be expected.

The kinetic rate data obtained in these studies do not allow a clear choice to be made between the two types of complexation discussed above. However two experimental results argue against complexation between the benzyl radical and the substituted aromatic ring at the other end of the molecule. First at least part of the time this pi complex would be expected to collapse to a sigma complex. After rearomatization this should yield the cyclized product shown in Figure 15. No evidence of this product could be observed. In obtaining the

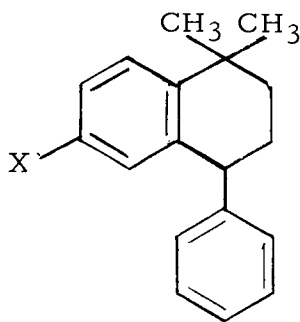


Figure 15. The cyclization product expected from an anchimerically assisted hydrogen abstraction from 4-methyl-1-phenyl-4-(substitutedphenyl)pentane.

relative rates of hydrogen abstraction for the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes it was possible to observe the disappearance of the benzylic hydrogen signal at about 2.4 δ and the appearance of the product benzylic hydrogen alpha to the bromine atom at about 4.5 δ . With each of the members of this series 90% or more of the starting material could be accounted for by the integration of these two signals. A second result that is difficult to explain if intramolecular complexation of the benzyl radical is important is the great difference in results observed for hydrogen abstraction by trichloromethyl radical and bromine atom from the α,ω -diphenylalkanes. Abstraction by either radical makes the same benzyl radical which should be stabilized similarly if this type of intramolecular complexation is important.

In conclusion, hydrogen abstraction by trichloromethyl radical from α,ω -diphenylalkanes shows that the distance between the two phenyl groups strongly influences the rate of reaction. Results of hydrogen abstraction by trichloromethyl radical from 1-phenylalkanes and results from hydrogen abstraction by bromine atoms from both α,ω -diphenylalkanes and 1-phenylalkanes suggest that this effect does not arise from simple steric or electronic effects. Hydrogen abstraction from 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes suggest that long range substituent effects strongly influence the rate of reaction. Relative rates of hydrogen abstraction by trichloromethyl

radical from the 1-phenyl-4-substitutedbutanes suggest that this influence is not a pure inductive effect. All these data can be explained by assuming that trichloromethyl radical can be complexed to an electron rich site in the substrate molecule. If the proper conformations are present this complexed free radical can then be intramolecularly transferred to the site of hydrogen abstraction.

EXPERIMENTAL

Procedures

Melting points were taken in unsealed capillary tubes with a Mel-Temp melting point apparatus. Boiling points and melting points are uncorrected. Nuclear magnetic resonance were taken on a Varian A-60 or a Varian HA-100 spectrometer with tetramethylsilane used as reference and carbon tetrachloride (Matheson Coleman and Bell or Mallinckrodt) or bromotrichloromethane (Matheson Coleman and Bell) used as solvents. Infrared spectra were taken on a Beckman IR-8 spectrophotometer, neat on sodium chloride plates or in carbon tetrachloride solution in a sodium chloride cell. Gas-liquid chromatographic analyses were carried out with a Varian 202-B gas chromatograph equipped with a linear temperature programmer and a Sargent recorder with disc integrater. The columns used in the gas chromatograph were 10 feet x 1/4 inch with 5% S.E. 30 on Chromosorb W. The gas chromatograph was equipped with thermal conductivity detectors. Helium was used as the carrier gas.

Purification of the Reagents

Purification of Bromotrichloromethane

Commercial bromotrichloromethane (Matheson Coleman and

Bell) was distilled and the fraction distilling over the range 103-104°C was collected.

Purification of Carbon Tetrachloride

Spectrophotometric grade carbon tetrachloride (Matheson Coleman and Bell or Mallinckrodt) was used without further purification.

Purification of Chlorobenzene

Commercial chlorobenzene (Matheson Coleman and Bell) was used without further purification.

Purification of o-Dichlorobenzene

Commercial o-dichlorobenzene was distilled and the fraction boiling between 179-181°C was collected.

Purification of Diphenylmethane

Commercial diphenylmethane (Matheson Coleman and Bell) was distilled and a constant boiling fraction was utilized which contained no impurities by gas-liquid chromatographic analysis.

Purification of N-Bromosuccinimide

Commercial N-bromosuccinimide was recrystallized from water.

Purification of 1-Phenylalkanes

Each 1-phenylalkane was obtained commercially and used without further purification.

Purification of 1,2-Diphenylethane

Commercial 1,2-diphenylethane was recrystallized from ethanol; m p. 50.8-52.2°C, lit. 52.5-53.0°C (73).

Preparation of Compounds

Preparation of 1,3-Diphenylpropane

1,3-Diphenyl-2-propanone (Columbia) was reduced by a Clemmensen reaction (74). The crude 1,3-diphenylpropane was distilled on a spinning band apparatus to give a product greater than 99% pure by gas-liquid chromatography; boiling point 116°C at 1.5 mm, lit. 124°C at 2 mm (75); $n_D^{20} = 1.5585$, lit. $n_D^{20} = 1.5594$ (76).

Preparation of 1,4-Diphenylbutane

Phenylcyanide was added to a solution of 3-phenylpropyl magnesium bromide. Work up gave 1,4-diphenyl-1-butanone (77) in 59% yield; m.p. 51-54°C. Reduction by the Huang-Minlon modification of the Wolff Kishner reaction (78), using the ketone, hydrazine hydrate, and potassium hydroxide in a 1:2:2 molar ratio, gave the crude

product in 64% yield. Recrystallization from ethanol gave 1,4-diphenylbutane; m.p. 51.8-53.2°C, lit. 52.0-52.5°C (79). The nmr spectrum confirmed the structure.

Preparation of 1,5-Diphenylpentane

Commercial 1,5-pentanedioyl dichloride was dissolved in benzene and this solution was slowly added to aluminum chloride suspended in a large excess of benzene. During addition the system was cooled in ice water. After stirring for two hours, during which time the system warmed to room temperature, the mixture was carefully added to ice and concentrated hydrochloric acid. After drying, removal of benzene left yellow crystals of 1,5-diphenyl-1,5-pentanedione.

1,5-Diphenyl-1,5-pentanedione was reduced to the desired hydrocarbon by the Huang-Minlon modification of the Wolff-Kishner reaction (78). The diketone, potassium hydroxide and hydrazine hydrate were reacted in a 1:4:4 ratio. The potassium hydroxide was dissolved in diethylene glycol. The diketone and hydrazine hydrate were added to the above solution and refluxed one hour. Water and unreacted hydrazine hydrate were then distilled off until the pot temperature reached 200°C. The solution refluxed at 200°C for six hours. After cooling, an excess of water was added to the clear gold solution. The product was extracted with ether. After drying with anhydrous magnesium sulfate, removal of solvent gave 1,5-diphenylpentane. The

product was distilled and a fraction with a boiling point of 114°C at 0.05 mm, lit. 196-200°C at 25 mm (80), was collected with

$$n_D^{21} = 1.5491.$$

Preparation of 1,6-Diphenylhexane

Wurtz coupling of 1-bromo-3-phenylpropane with sodium metal gave 1,6-diphenylhexane in 19% yield; b. p. 121°C at .1 mm, lit.

345°C at 760 mm (81). Distillation on the spinning band apparatus

gave a product greater than 99% pure with $n_D^{20} = 1.5412$, lit.

$$n_D^{20} = 1.5409 \text{ (81)}.$$

Preparation of 1,7-Diphenylheptane

Heptanedioic acid was added to thionyl chloride. Refluxing of the solution, followed by removal of the thionyl chloride, gave heptanedioyl dichloride. 1,7-Diphenylheptane was obtained from this compound by the same procedure as outlined above for 1,5-diphenylpentane in 32% yield; b. p. 129°C at 0.05 mm to 145°C at 0.03 mm;

100% pure by gas-liquid chromatograph; $n_D^{23} = 1.5351$.

Analysis. Calculated for $C_{19}H_{24}$. C, 90.42%; H, 9.48%.

Found C, 90.42%; H, 9.48%.

Preparation of 1,8-Diphenyloctane

1,8-Octanedioic acid was converted to the corresponding

dichloride by refluxing with thionyl chloride. Reaction of this compound by the same procedure as outlined above for 1,5-diphenylpentane gave 1,8-diphenyloctane in 29% yield; b. p. 151-157°C at 0.35 mm; $n_D^{21} = 1.5337$. The nmr spectrum helped to confirm the structure.

Preparation of 1,9-Diphenylnonane

Refluxing with thionyl chloride converted 1,9-nonanedioic acid to the corresponding dichloride. Reaction of this compound by the same procedure as outlined above for 1,5-diphenylpentane gave 1,9-diphenylnonane in 45% yield; 100% pure by gas-liquid chromatography; $n_D^{21} = 1.5297$.

Preparation of 1,10-Diphenyldecane

Refluxing with thionyl chloride converted 1,10-decanedioic acid to the corresponding dichloride. Reaction of this compound by the same procedure as outlined above for 1,5-diphenylpentane gave 1,10-diphenyldecane as a yellow oil; 100% pure by gas-liquid chromatography; $n_D^{20} = 1.5272$, lit. $n_D^{20} = 1.5282$ (82).

Preparation of 4-Methyl-1,4-diphenylpentane

Neophyl chloride, (2-chloro-1,1-dimethylethyl)benzene, was prepared by the addition over 7 hours of 2.2 moles of distilled methallyl chloride to 10 moles of dry benzene containing about

0.4 moles of concentrated sulfuric acid (83). The methally chloride was added rapidly at the beginning of the addition, then the rate was slowed toward the end. During addition the whole system was cooled in ice water. Then it was allowed to warm to room temperature while stirring overnight. Work-up and distillation (66°C at 0.3 mm) gave 90% yield of product.

Addition of an ether solution containing 0.4 moles of neophyl chloride to 1.5-fold excess of magnesium turnings in ether, followed by two and one-half hours of refluxing, produced neophyl magnesium chloride. A solution of 0.4 moles of phenylacetaldehyde was slowly added over 5 hours to the ethereal solution of neophyl magnesium chloride. After stirring overnight and standard Grignard reaction work-up, 0.35 moles of crude 4-methyl-1,4-diphenyl-2-pentanol were obtained. This product was contaminated with about 10% of a compound believed to be 2,5-dimethyl-2,5-diphenylhexane. This compound probably formed from coupling of the Grignard reagent.

A solution of 0.2 moles of the crude alcohol from above, dissolved in benzene, was slowly added to a solution containing 0.35 moles of potassium dichromate, 76 ml. acetic acid, 136 ml. concentrated sulfuric acid and 450 ml. of water (84). The whole mixture was stirred overnight. After work up 0.134 moles of crude 4-methyl-1,4-diphenyl-2-pentanone was obtained. Distillation on a spinning band column gave the product in 96% purity by gas-liquid chromatography.

The 2,5-dimethyl-2,5-diphenylhexane impurity was completely removed at this point.

Reduction by the Huang-Minlon modification of the Wolff-Kishner reaction (78) gave 4-methyl-1,4-diphenylpentane. A solution containing 0.05 moles of the above ketone and 0.20 moles of hydrazine hydrate dissolved in diethylene glycol was refluxed for 45 minutes. Then, to this solution was added a solution of 0.20 moles of potassium hydroxide dissolved in 100 ml. diethylene glycol. This new solution was refluxed one hour. The apparatus was rearranged for distillation and 6 ml. of liquid removed. At this point the pot temperature was 200°C. The distillation head was removed and refluxing continued for 3 hours. After standard work-up, 0.028 moles of 4-methyl-1,4-diphenylpentane were obtained. The product was 99% pure by gas-liquid chromatographic analysis. The nmr spectrum consisted of a multiplet centered at about 7.1 δ for the aromatic protons, a triplet centered at about 2.4 δ for the benzylic protons, a multiplet spread from about 1.7 δ to 1.2 δ for the other methylene protons, and a singlet at 1.2 δ for the methyl protons. The relative peak areas are approximately 10:2:4:6. See Table 11 for a summary of the physical properties of this compound.

Preparation of 4-(4-Aminophenyl)-4-methyl-1-phenylpentane

Addition of 4-methyl-3-penten-2-one to a cold mixture of anhydrous aluminum chloride and benzene gave

4-methyl-4-phenyl-2-pentanone in 63% yield (85).

The Kindler modification of the Willgerodt reaction was used to obtain 4-methyl-4-phenyl-pentanoic acid from the above ketone (86). A mixture of 2.6 moles of the ketone, 4.1 moles of sulfur, and 4.3 moles of morpholine was refluxed 22 hours. While still warm, the mixture was poured into 550 ml. ethanol and 1.25 moles of the 4-methyl-4-phenylpentanethiomorpholide were recovered. This product was mixed with 2.0 liters of concentrated hydrochloric acid and refluxed 48 hours (87). After work-up, 0.458 moles of 4-methyl-4-phenylpentanoic acid were obtained; b. p. 120° C at 20 mm.

To 2 liters of concentrated nitric acid were added 0.46 moles of the 4-methyl-4-phenylpentanoic acid, and the solution was stirred overnight (88). The solution was poured onto ice and extracted with benzene. The product, 4-methyl-4-(4-nitrophenyl)pentanoic acid, was obtained in 57% yield from this step; m. p. 110-113° C.

To 100 ml. of thionyl chloride were added 0.095 moles of 4-methyl-4-(4-nitrophenyl)pentanoic acid. The solution was refluxed for 5 hours, and then the thionyl chloride was removed. The product, a yellow oil, was dissolved in 100 ml. benzene and added to a mixture of 1000 ml. of benzene and 0.19 moles of anhydrous aluminum chloride. During addition the whole system was cooled in ice, then was allowed to warm to room temperature while stirring overnight. The reaction mixture was worked up as usual for an acylation. The organic layer

was extracted with base to remove any unreacted starting material. After the organic solvent was removed, 4-methyl-4-(4-nitrophenyl)-1-phenyl-1-pentanone was obtained as a waxy solid in 77% yield. The nmr spectrum of this compound consisted of a doublet centered at 8.05 δ for the two aromatic protons ortho to the nitro group, a multiplet of peaks centered at 7.48 δ for the rest of the aromatic protons, a triplet centered at 2.6 δ for the protons on the carbon α to the ketone, a triplet centered at 2.1 δ for the protons on the carbon β to the ketone, and a singlet 1.4 δ for the protons in the two methyl groups. The relative peak areas were approximately 2:7:2:2:6.

Reduction by the Huang-Minlon modification of the Wolff-Kishner reaction reduces ketones to hydrocarbons and aromatic nitro substituents to amines (89). A solution of 0.43 moles of hydrazine hydrate and 0.07 moles 4-methyl-4-(4-nitrophenyl)-1-phenyl-1-pentanone, dissolved in diethylene glycol, was refluxed for 30 minutes. To this solution was added over 20 minutes a solution of 0.43 moles of potassium hydroxide dissolved in diethylene glycol. The resulting solution was refluxed 30 minutes. The apparatus was rearranged for distillation and 22 ml. of liquid removed. The pot temperature reached 180°C. The distillation head was removed and refluxing was continued for about 3 hours during which time the color changed from dark brown to light yellow. Work-up gave crude 4-(4-aminophenyl)-4-methyl-1-phenylpentane. The nmr spectrum was very useful in

identifying this compound. The nmr spectrum consisted of a multiplet of peaks centered at 7.0 δ for 7 aromatic protons, a doublet centered at 6.4 δ for 2 aromatic protons ortho to the amino function, a rather broad singlet at 3.1 δ for the protons on nitrogen of the amino function, a triplet centered at about 2.4 δ for the benzylic protons, a multiplet of peaks from 1.8 δ to 1.2 δ for the nonbenzylic methylene protons, and a singlet at 1.2 δ for the methyl protons. The relative peak areas were approximately 7:2:2:2:4:6.

Preparation of 4-Methyl-4-(4-nitrophenyl)-1-phenylpentane

This compound was obtained from 4-(4-aminophenyl)-4-methyl-1-phenylpentane by oxidation of the amino substituent to a nitro substituent. A first attempt with peroxyfluoroacetic acid gave only black tar (90). However, oxidation with peracetic acid, carefully following the procedure of Emmons (91), gave the desired compound in 10% yield; 97% pure by gas-liquid chromatography. Please see Table 11 for physical constants and elemental analysis. The nmr spectrum consisted of a doublet centered at 8.0 δ for the aromatic protons ortho to the nitro substituent, a doublet centered at 7.3 δ for the protons meta to the nitro substituent, a multiplet centered at 7.05 δ for the rest of the aromatic protons, a triplet centered at 2.5 δ for the benzylic protons, a multiplet spread from 1.7 δ to 1.2 δ for the methylene protons, and a singlet at 1.1 δ for the methyl protons.

The relative peak areas were approximately 2:2:5:2:4:6.

Preparation of the 4-(4-Chlorophenyl)-4-methyl-1-phenylpentane

Glacial acetic acid was used to dissolve 4-(4-aminophenyl)-4-methyl-1-phenylpentane. This solution was slowly added to a solution of sodium nitrite dissolved in concentrated sulfuric acid. During addition the system was cooled in an ice bath. To this solution of diazonium ions was rapidly added a solution of cuprous chloride dissolved in hydrochloric acid. The ice bath was then removed and the system stirred for two and one-half hours. The solution was then heated for 35 minutes. After cooling, the mixture was extracted with a solution of benzene and hexane. This solution was washed with water, 20% potassium hydroxide, and finally again with water. Removal of the solvent left an oil that was shown to be a mixture by gas-liquid chromatographic analysis. Repeated distillation at last gave 4-(4-chlorophenyl)-4-methyl-1-phenylpentane in 7% yield; 97% pure by gas-liquid chromatography. See Table 11 for a summary of the physical properties of this molecule. The nmr spectrum of this compound consisted of a multiplet centered at 7.1 δ for the aromatic protons, a triplet at 2.4 δ for the benzylic protons, a multiplet from 1.7 δ to 1.2 δ for the methylene protons, and a singlet at 1.2 δ for the methyl protons. The relative peak areas were approximately 9:2:4:6.

Preparation of the 4-(4-Bromophenyl)-4-methyl-1-phenylpentane

A mixture of 0.1 mole of 4-(4-aminophenyl)-4-methyl-1-phenylpentane and 250 ml. of 48% hydrobromic acid was stirred and was cooled in an ice bath. To this mixture a solution of 0.3 moles of sodium nitrite, dissolved in 25 ml. of water, was added. Upon mixture of these two solutions, a blackish brown tar was formed that could not be stirred. After 20 minutes of stirring this tarry mixture, a solution of 0.13 moles of cuprous bromide dissolved in 50 ml. of 48% hydrobromic acid was added. The mixture was stirred in an ice bath for 1 hour and then allowed to warm to room temperature. The mixture was then heated for 2 hours. It was then cooled and extracted with benzene. This solution of the product in benzene was extracted with base, washed until neutral, and then dried over anhydrous magnesium sulfate. Removal of the solvent left a reddish black oil. The nmr of this oil suggested that the mixture contained at least some of the desired compound. A crude separation was accomplished by adding the mixture to an alumina column and then eluting with hexane and benzene. The mixture was next distilled several times until after the last distillation it was 98% pure by gas-liquid chromatography. However, the nmr of this material clearly indicated the presence of at least 15% of the starting material. The mixture was added to a column of 80-200 mesh activated alumina (Matheson Coleman and Bell) and

eluted with hexane. 4-(4-Bromophenyl)-4-methyl-1-phenylpentane was obtained in 5% overall yield; 97% pure as indicated by analysis by both nmr and gas-liquid chromatograph. See Table 11 for a summary of the physical properties of this compound. The nmr spectrum consisted of a doublet centered at 7.3 δ for the aromatic protons ortho to the bromo atom, a multiplet centered at 7.1 δ for the rest of the aromatic protons, a triplet centered at 2.4 δ for the benzylic protons, a multiplet from 1.8 δ to 1.2 δ for the methylene protons, and a singlet at 1.2 δ for the methyl protons. The relative peak areas were approximately 2:7:2:4:6.

Preparation of 4-(2-Methoxyphenyl)-4-methyl-1-phenylpentane

To a solution of anisole and concentrated sulfuric acid was added a solution of one mole of methally chloride dissolved in anisole (92). After stirring overnight, work-up and distillation on a spinning band column gave 0.13 moles of 1-chloro-2-(2-methoxyphenyl)-2-methylpropane and 0.056 moles of 1-chloro-2-(4-methoxyphenyl)-2-methylpropane. Corrosion of the spinning band column was observed during the distillation. The nmr for the ortho substituted compound gave a triplet centered at 7.2 δ for the protons meta to the methoxy group, a triplet at 6.8 for the protons ortho and para to the methoxy group, a singlet at 3.9 δ for the methylene protons alpha to the chloride atom, a singlet at 3.8 δ for protons on the methoxy group,

and a singlet at 1.5 δ for the methyl protons. The ratio of the peak areas was approximately 2:2:2:3:6. Less than 5% of the para-substituted product was mixed with the ortho-substituted product. The nmr for the para-substituted compound gave a doublet centered at 7.2 δ for the protons meta to the methoxy substituent, a doublet centered at 6.8 δ for the protons ortho to the methoxy substituent, a singlet at 3.8 δ for the protons on the methoxy substituent, a singlet at 3.5 δ for the protons on the carbon alpha to the chlorine atom, and a singlet at 1.4 δ for the methyl protons. The ratio of the peak areas was approximately 2:2:3:2:6. No ortho-substituted product was observed in the para-substituted product.

The 4-(2-methoxyphenyl)-4-methyl-1-phenylpentane compound was synthesized from the 1-chloro-2-(2-methoxyphenyl)-2-methylpropane. Addition of an ether solution containing 0.13 moles of this compound to an equimolar amount of magnesium turnings in ether, following by 8.5 hours of refluxing, produced the corresponding Grignard reagent. To an ethereal solution of this Grignard reagent was added an ethereal solution of 0.19 moles of phenylacetaldehyde. After refluxing overnight, work-up of the reaction mixture gave 0.10 moles of crude 4-(2-methoxyphenyl)-4-methyl-1-phenyl-2-pentanol.

This alcohol was dissolved in 435 ml. of benzene and slowly added over 2.5 hours to a cold solution of 60 g. of sodium dichromate,

45 ml. of glacial acetic acid, 78 ml of concentrated sulfuric acid and 258 ml. of water (84). After work-up a mixture was obtained containing about 80% 4-(2-methoxyphenyl)-4-methyl-1-phenyl-2-pentanone.

4-(2-Methoxyphenyl)-4-methyl-1-phenyl-2-pentanone was reduced to the hydrocarbon by use of the Huang-Minlon modification of the Wolff-Kishner reaction (78). The crude ketone, hydrazine hydrate, and potassium hydroxide in the molar ratio of 1:3:4.5 were dissolved in diethylene glycol and refluxed for 2 5 hours. Water was then removed by distillation until the temperature reached 230°C. The system was refluxed at this temperature overnight. Work-up gave a mixture of products. The infrared spectrum of the main product indicated that not only had the ketone been reduced but that the product contained a hydroxy substituent. The Huang-Minlon modification of the Wolff-Kishner reaction will convert a methoxyphenyl substituent into a hydroxyphenyl substituent (93).

Remethylation of 4-(2-hydroxyphenyl)-4-methyl-1-phenylpentane was accomplished with dimethyl sulfate (94). The substrate was dissolved in ethanol. This solution was mixed with a 2 N sodium hydroxide solution and the resulting solution was heated to 40-45°C. To this solution was slowly added dimethyl sulfate. After heating for one hour at 55°C, the reaction was worked up giving a red oil containing the desired 4-(2-methoxyphenyl)-4-methyl-1-phenylpentane in about 90% purity. Further purification of this compound was

attempted by adding the product to a column of 80-200 mesh activated alumina (Matheson Coleman and Bell) and eluting with hexane and carbon tetrachloride. This process improved the purity and was repeated a second time. About 1.5 g of product was obtained in overall yield of 5%; purity 98% by gas-liquid chromatography. See Table 11 for a summary of physical properties. The nmr spectrum consisted of a multiplet at 7.1 δ for most of the aromatic protons, a triplet centered at 6.7 δ for the aromatic protons ortho and para to the methoxy group, a singlet at 3.8 δ for the protons on the methoxy substituent, a triplet centered at 2.5 δ for the benzylic protons, a multiplet centered at 1.8 δ for two methylene protons, and a multiplet centered at 1.3 δ with a singlet at 1.3 δ on top of it for the other aliphatic protons. The relative peak areas were approximately 7:2:3:2:2:8.

Preparation of 4-(4-Methoxyphenyl)-4-methyl-1-phenylpentane

This compound was prepared in the same manner as outlined above for 4-(2-methoxyphenyl)-4-methyl-1-phenylpentane. 0.056 Moles of 1-chloro-2-(4-methoxyphenyl)-2-methylpropane, synthesized as outlined above, gave about 0.002 moles, 4% overall yield, of 4-(4-methoxyphenyl)-4-methyl-1-phenylpentane. Purification first by adding the product to a column of 80-200 mesh activated alumina (Matheson Coleman and Bell) and eluting with hexane and benzene followed by distillation gave the compound; purity 96.8% by gas-liquid

chromatographic analysis. See Table 11 for summary of physical properties of this compound. The nmr spectra consisted of a multiplet centered at 7.0 δ for 7 aromatic protons, a doublet centered at 6.7 δ for the 2 aromatic protons ortho to the methoxy group, a singlet at 3.6 δ for the protons on the methoxy substituent, a triplet centered at 2.4 δ for the benzylic protons, a multiplet from 1.7 δ to 1.2 δ for the methylene protons, and a singlet at 1.2 δ for the methyl protons. The relative peak areas were 7:2:3:2:4:6.

Preparation of 4-Methyl-4-(4-methylphenyl)-1-phenylpentane

To a solution of toluene and concentrated sulfuric acid was added a solution of methallyl chloride dissolved in toluene (83). During addition the system was cooled in ice water, then it was allowed to warm to room temperature while stirring was continued overnight. Work-up and distillation (90°C at 0.20 mm) gave 4-(2-chloro-1,1-dimethylethyl)toluene in 70% yield. Both the nmr spectrum and analysis by gas-liquid chromatography suggested the presence of about 10% ortho isomer (92).

Addition of an ether solution containing the above product to magnesium turnings, followed by 6 hours of refluxing, produced the desired Grignard reagent. To an ethereal solution of this Grignard reagent was added a solution of phenylacetaldehyde. After refluxing overnight and standard Grignard reaction work up, crude

4-methyl-4-(4-methylphenyl)-1-phenyl-2-pentanol was obtained.

A solution containing 0.31 moles of the above alcohol was dissolved in 1000 ml. of benzene and slowly added to a mixture containing 166 g. of sodium dichromate, 120 ml. of glacial acetic acid, 225 ml. of sulfuric acid and 750 ml. of water (84). The mixture was stirred overnight and work up gave crude 4-methyl-4-(4-methylphenyl)-1-phenyl-2-pentanone.

Without further purification the crude product above was reduced by the Huang-Minlon modification of the Wolff-Kishner reaction (78) to give crude 4-methyl-4-(4-methylphenyl)-1-phenylpentane. Purification was difficult, but repeated distillation gave the desired product. Gas-liquid chromatography suggested the presence of eight percent of the ortho isomer of this compound. The nmr spectrum, unlike the case for the methoxy derivatives, however, did not exhibit a separate set of signals for this possible impurity. The physical constants for this compound are listed in Table 11. The nmr spectrum consists of a multiplet centered at 7.0 δ for the aromatic protons, a triplet centered at 2.4 δ for the methylene benzylic protons, a singlet at 2.2 δ for the methyl benzylic protons, a multiplet from 1.7 δ to 1.2 δ for the methylene protons, and a singlet at 1.2 δ for the methyl protons. The relative areas of these peaks were approximately 9:2:3:4:6.

Table 11. Physical properties of the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes.

Substituent	b. p., °C	n_D^{20}	Formula	% Carbon		% Hydrogen		% Other	
				Calc.	Found	Calc.	Found	Calc.	Found
H	105° C at 0.2 mm	1.5481	C ₁₈ H ₂₂	90.69	90.57	9.31	9.27		
p-NO ₂	150° C at 0.1 mm	1.5690	C ₁₈ H ₂₁ NO ₂	76.29	76.10	7.47	7.59	4.94	4.85
p-Cl	105° C at 0.1 mm	1.5568	C ₁₈ H ₂₁ Cl	79.24	79.15	7.76	7.78	12.99	13.05
p-Br	120° C at 0.1 mm	1.5690	C ₁₈ H ₂₁ Br	68.14	68.20	6.67	6.72	25.19	25.09
o-CH ₃ O	---	1.5480	C ₁₉ H ₂₄ O	---	---	---	---	---	---
p-CH ₃ O	110° C at 0.05 mm	1.5498	C ₁₉ H ₂₄ O	85.02	84.85	9.01	8.95		
p-CH ₃	103° C at 0.1 mm	1.5442	C ₁₉ H ₂₄	90.42	90.36	9.58	9.66		

Preparation of 1-Chloro-4-phenylbutane

Reduction of 4-phenylbutanoic acid with lithium aluminum halide gave 4-phenyl-1-butanol. Treatment of this compound with thionyl chloride gave 1-chloro-4-phenylbutane; 98% pure by gas-liquid chromatographic analysis; b. p. 76°C at .24 mm, lit. 112-123°C at 17 mm (88); $n_D^{21} = 1.5197$.

Preparation of 5-Phenylpentanonitrile

Refluxing of 1-chloro-4-phenylbutane with sodium cyanide gave the desired product; 99% pure by gas-liquid chromatography; b. p. 98°C at .09 mm, lit., 152°C at 13 mm (95); $n_D^{21} = 1.5119$.

Preparation of 1-Methoxy-4-phenylbutane

Refluxing of 1-chloro-4-phenylbutane with sodium methoxide in methanol gave the desired product; 98% pure by gas-liquid chromatographic analysis; b. p. 53-55°C at 1.5 mm; n_D^{21} of 1.4950.

Preparation of Ethyl 5-Phenylpentanoate

A solution of 5-phenylpentanoic acid and ethanol, in the presence of sulfuric acid, was refluxed. The desired product was obtained; 100% pure by gas-liquid chromatographic analysis; b. p. 137-138°C at 5 mm, lit., 157-160°C at 18 mm (96); $n_D^{21} = 1.4913$.

Product Studies

The Reaction of 1-Phenylalkanes with N-Bromosuccinimide; Initiated with Light

Reaction of 1-phenylalkanes with N-bromosuccinimide gave only benzylic bromination. An nmr of the solution from the reaction of 1-phenylbutane with this reagent showed a triplet centered at 2.6 δ for the benzylic protons of 1-phenylbutane and a triplet centered at 4.8 δ for the benzylic proton on the carbon alpha to the bromine atom in 1-bromo-1-phenylbutane. A nmr spectrum of the solution from the reaction of 1-phenylheptane with N-bromosuccinimide showed a triplet centered at 2.6 δ due to the benzylic protons of 1-phenylheptane and a triplet centered at 4.8 δ for the benzylic proton on the carbon alpha to the bromine atom in 1-bromo-1-phenylheptane. In both these nmr's no evidence of any other products could be found. Since independent measurements indicate that as little as five mole-percent of a non-benzylic secondary bromide could be detected in our reaction mixtures by nmr, it can be assumed that at least 95% of the reaction was at the benzylic position.

The Reaction of α,ω -Diphenylalkanes with N-Bromosuccinimide; Initiated with Light

Reaction of α,ω -diphenylalkanes with N-bromosuccinimide gave only benzylic bromination. An nmr spectrum of the solution from the

reaction of 1,6-diphenylhexane with this reagent showed a triplet centered at 2.5 δ for the benzylic protons of 1,6-diphenylhexane and a triplet centered at 4.5 δ for the benzylic proton on the carbon bonded to the bromine atom in 1-bromo-1,6-diphenylhexane. No evidence for any other products could be observed. Since again independent measurements indicate that as little as five mole-percent of a non-benzylic secondary bromide could be detected in our reaction mixtures by nmr, it can be concluded that at least 95% of the reaction was at the benzylic position.

The Reaction of 1-Phenylalkanes with Bromotrichloromethane; Initiated with Light

Reaction of 1-phenylalkanes with bromotrichloromethane gave only benzylic bromination. A solution consisting of 4.73 g. (29.16 mmoles) of 1-phenylhexane and 35.42 g. (178.6 mmoles) of bromotrichloromethane was placed in a pyrex flask equipped with a condenser. The flask was placed in an oil bath maintained at 70°C and irradiated with a 275 watt Ken-Rad sunlamp for 3 hours and 50 minutes. During this time the system was swept out with nitrogen gas. After reaction an nmr spectrum was obtained which showed a triplet centered at 2.4 δ for the benzylic protons of 1-phenylhexane and a triplet centered at 4.8 δ for the benzylic proton on the carbon bonded to the bromine atom in the product, 1-bromo-1-phenylhexane.

The relative areas of these peaks were 10.6:8.6. Since no evidence for other products could be observed in the nmr, the relative areas of the two benzylic peaks allowed the calculation of the number of grams of 1-bromo-1-phenylhexane formed (4.37 grams, 18.11 mmoles) and the number of grams of 1-phenylhexane left (1.79 grams, 11.04 mmoles). The reaction mixture was distilled and several fractions were collected. Since the distillation did not cleanly separate the reactant and the product, the concentration of each compound in each fraction was determined from the nmr spectrum. By this method 1.82 grams (11.22 mmoles) of 1-phenylhexane were recovered and 4.02 grams (16.67 mmoles) of 1-bromo-1-phenylhexane were recovered. The total amount of material recovered from the reaction accounts for 95.7% of the theoretical amount.

Fraction 4 above was redistilled and gave pure 1-bromo-1-phenylhexane with b. p. of 60°C at 0.04 mm; $n_D^{28} = 1.5258$. This compound was independently prepared by reaction of phenyl magnesium bromide with hexanal followed by treatment of the alcohol with phosphorus tribromide. This product had a b. p. of 68-75°C at 0.15 mm; $n_D^{32.8} = 1.5252$. The nmr spectrum consisted of a multiplet centered at 7.2 δ for the aromatic protons, a triplet at 4.8 δ for the proton on the carbon atom bonded to the bromine atom, a multiplet centered at 2.2 δ for the methylene protons on carbon 2, a multiplet centered at 1.7 δ for the methylene protons on carbons 3-5, and a

triplet centered at 0.8 δ for the methyl group. This nmr spectrum was identical to that observed for the bromide product of the reaction of bromotrichloromethane and 1-phenylhexane discussed above.

An additional example of the reaction of 1-phenylalkanes with bromotrichloromethane is as follows. A solution consisting of 4.89 grams (25.71 mmoles) of 1-phenyloctane and 50.58 grams (255.07 mmoles) of bromotrichloromethane was added to a pyrex flask equipped with a condenser. The flask was placed in an oil bath maintained at 70°C and irradiated with a 275 watt Ken-Rad sunlamp for 4 hours. The system was purged with nitrogen before reaction. After reaction an nmr was obtained which showed a triplet centered at 2.5 δ from the benzylic protons of 1-phenyloctane and a triplet centered at 6.8 δ from the benzylic proton on the carbon bonded to the bromine in the product, 1-bromo-1-phenyloctane. The relative areas of these two peaks were 8.5:5.0. Since no evidence for other products could be observed in the nmr, the relative areas of the two benzylic peaks were used to calculate the number of grams of 1-bromo-1-phenyloctane formed; 3.74 grams (13.90 mmoles) and the number of grams of 1-phenyloctane left; 2.25 grams (11.81 mmoles). The reaction mixture was distilled and three fractions were collected. As determined by nmr analysis, the first fraction was pure 1-phenyloctane, the second fraction was a mixture of 1-phenyloctane and 1-bromo-1-phenyloctane, and the third fraction was pure

1-bromo-1-phenyloctane. The nmr spectrum allowed the amount of each compound in fraction 2 to be determined.

In the three fractions 1.92 grams (10.10 mmoles) of 1-phenyloctane was recovered and 3.64 grams (13.52 mmoles) of 1-bromo-1-phenyloctane were recovered. The total amount of material recovered from the reaction accounts for 91.8% of the theoretical yield. The 1-bromo-1-phenyloctane had an nmr spectrum consisting of a multiplet centered at 7.3 δ for the aromatic hydrogens, a triplet centered at 4.85 δ for the proton bonded to the same carbon atom as the bromine atom, a multiplet centered at 2.1 δ for the methylene protons on carbon 2, a multiplet centered at 1.1 δ for the rest of the methylene protons, and a triplet centered at 0.8 for the methyl protons. This compound had a b.p. of 92-96°C at about 0.1 mm and a $n_D^{21} = 1.5223$.

The Reaction of α,ω -Diphenylalkanes with Bromotrichloromethane; Initiated with Light

Reaction of α,ω -diphenylalkanes with bromotrichloromethane gave only benzylic bromination. Bromotrichloromethane and 1,4-diphenylbutane in the molar ratio of 5.5:1 were irradiated with a 275 watt Ken-Rad sunlamp at 73°C. An nmr spectrum of the reaction mixture showed a multiplet centered at 8.1 δ for the aromatic protons; a triplet centered at 4.85 δ for the proton on the carbon alpha to

bromide in the product, 1-bromo-1,4-diphenylbutane; a triplet at 2.6 δ for the benzylic protons of the reactant, 1,4-diphenylbutane; a multiplet centered at 2.2 δ for the methylene protons on the carbon beta to carbon 1 in the product, and a multiplet centered at 1.6 δ for the other methylene protons in both the reactant and the product. No other peaks could be observed in the nmr.

An nmr spectrum of the reaction mixture of a solution of 1,6-diphenylhexane and diphenylmethane in bromotrichloromethane after irradiation with a 275 watt Ken-Rad sunlamp showed only two products, 1-bromo-1,2-diphenylmethane, characterized by a singlet at 6.1 δ for the proton bonded to the carbon alpha to bromine and 1-bromo-1,6-diphenylhexane, characterized by two triplets on top of each other centered at 4.80 δ and 4.78 δ for the proton bonded to carbon 1. No other bromination products could be observed. Using the nonbenzylic methylene protons of 1,6-diphenylhexane as a nmr standard, 91% of the theoretical integration for the benzylic protons of 1,6-diphenylhexane can be accounted for by the signals at 4.8 δ and 2.5 δ .

The Reaction of 4-Methyl-1-phenyl-4-(substitutedphenyl)pentanes with Bromotrichloromethane; Initiated with Light

Only benzylic bromination was observed in the reaction of 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes with

bromotrichloromethane. An nmr spectrum of a reaction mixture of any of these compounds and diphenylmethane in bromotrichloromethane after irradiation with a 275 watt Ken-Rad sunlamp showed a singlet at 6.1 δ for the proton bonded to the carbon alpha to bromine in 1-bromo-1,2-diphenylmethane, a poorly resolved triplet centered at approximately 4.7 δ from the proton bonded to carbon 1 in the 1-bromo-4-methyl-1-phenyl-4-(substitutedphenyl)pentane, a singlet at 3.9 δ for the benzylic protons on diphenylmethane, and a triplet centered at approximately 2.5 δ for the benzylic protons in the 4-methyl-1-phenyl-4-(substituted phenyl)pentane. This much of the nmr spectrum of reaction mixtures of diphenylmethane and any of the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes were very similar. Using the methyl protons of the latter compounds as internal nmr standards, every compound in this series showed over 90% material balance. The ratio of the combined areas of the unreacted benzylic protons (c. a. 2.5 δ) and product benzylic protons (c. a. 4.8 δ), after statistical correction, was found to be approximately one third of the area of the internal standard.

A solution consisting of 2.96 grams (12.41 mmoles) of 4-methyl-1,4-diphenylpentane in 22.76 grams (114.82 mmoles) of bromotrichloromethane was placed in each of eight pyrex ampoules. The ampoules were cooled to dry ice-acetone temperature, evacuated, filled with N_2 at a reduced pressure, and sealed. The ampoules were

placed horizontally just below the surface of a mineral oil constant temperature bath maintained at $70.0 \pm 0.5^\circ\text{C}$. The samples were irradiated with a Ken-Ray sunlamp placed 20 cm above the surface of the oil for approximately 4.5 hours. An nmr spectra of the reaction mixture consisted of a multiplet centered at 7.2δ for the aromatic protons, a poorly resolved triplet at 4.65δ for the proton on the carbon alpha to the bromine atom, a triplet at 2.25δ for the benzylic protons of the starting material, a multiplet from 2.05δ to 1.1δ for the non-benzylic methylene protons of both the reactant and the product, and a doublet at 1.1δ for the methyl protons for both of these compounds. The ratio of the peak areas due to the benzylic protons of the product and the reactant was 11.2:2.6, respectively. These data allow the calculation of the number of grams of 1-bromo-4-methyl-1,4-diphenylpentane formed, 3.09 grams (9.76 mmoles); and the number of grams of 4-methyl-1,4-diphenylpentane left, 0.63 g (2.66 mmoles). This calculation would thus predict a total weight of 3.72 g of reactant and product. The bromotrichloromethane was removed from the reaction mixture by vacuum distillation leaving 3.56 grams of a light yellow oil; 95.6% of the theoretical amount necessary for a material balance.

The Reaction of 1-Phenyl-4-substitutedbutanes with Bromotrichloro-
methane; Initiated with Light

Only benzylic bromination products were observed in the reaction of 1-phenyl-4-substitutedbutanes with bromotrichloromethane. The results with 1-phenylbutane have been discussed above.

Ethyl 5-phenylpentanoate and 5-phenylpentanonitrile might be expected to show significant reactivity toward hydrogen abstraction from the carbon alpha to the carboxylate or cyano group. These groups should be able to stabilize the developing radical by resonance (96, 97). No evidence for this type of product could be observed.

Procedure for Kinetic Runs

Procedure for Kinetic Runs for the Reaction of Bromotrichloro-
methane with 1-Phenylalkanes

Solutions of two 1-phenylalkanes, o-dichlorobenzene, and bromotrichloromethane were prepared in the approximate molar ratios of 1:1:1:5. Approximately 0.75 ml of the solution was put in each of several pyrex ampoules. The ampoules were cooled to dry ice-acetone temperature, evacuated, filled with nitrogen gas, and then warmed to room temperature. This process was repeated three times. Then, after cooling and evacuation, the tubes were 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 $70.0 \pm 0.5^\circ\text{C}$. The samples were irradiated with ultraviolet light provided by a Ken-Rad 275 watt sunlamp placed 20 cm above the surface of the oil. Reaction times varied from three to ten hours, by which time 20% to 80% of the total hydrocarbons had reacted. The ampoules were then cooled and opened. Analysis of the mixtures both before and after reaction was carried out via gas-liquid partition chromatography on a ten foot by 1/4 inch column with 5% S. E. 30 on Chromosorb W.

All determinations were run in replicate. Most compounds were competed directly against 1-phenylethane. In certain cases, however, to insure maximum separation it was necessary to compete against a reference compound other than 1-phenylethane. For example it was necessary to compete 1-phenylpropane against 1-phenylnonane due to similarity of its retention time with that of 1-phenylethane. The rate constant obtained in these cases could be easily converted to a rate constant relative to 1-phenylethane. This conversion is illustrated in Equation 8 for the example given above of 1-phenylpropane where 1-phenylnonane was used as the reference.

$$\frac{k_{1\text{-phenylpropane}}}{k_{1\text{-phenylethane}}} = \frac{k_{1\text{-phenylpropane}}}{k_{1\text{-phenylnonane}}} \times \frac{k_{1\text{-phenylnonane}}}{k_{1\text{-phenylethane}}} \quad (8)$$

Procedure for Kinetic Runs for the Reaction of Bromotrichloromethane with the α,ω -Diphenylalkanes

Solutions of two α,ω -diphenylalkanes, o-dichlorobenzene, and bromotrichloromethane were prepared in the approximate molar ratios of 1:1:1:9. The rest of the procedure was as outlined above for the 1-phenylalkanes. In most cases, the compounds were compared directly against 1,2-diphenylethane. Where this was not possible a conversion as illustrated in Equation 8 above was used to obtain the rate relative to this compound.

Procedure for Kinetic Runs for the Reaction of N-Bromosuccinimide with 1-Phenylalkanes

The procedure was identical to that described above except that the solid N-bromosuccinimide was first introduced into the ampoule, followed by a solution of the two hydrocarbons and o-dichlorobenzene dissolved in carbon tetrachloride. The two hydrocarbons, o-dichlorobenzene and N-bromosuccinimide were in the approximate molar ratio of 1:1:1:1. Carbon tetrachloride was present in about an eight-fold molar excess of any other reagent. The reaction times varied from one to two hours, by which time 20% to 60% of the total hydrocarbons had reacted. All analytical details were analogous to those using bromotrichloromethane as the radical source.

Procedure for the Kinetic Runs for the Reaction of
N-Bromosuccinimide with α,ω -Diphenylalkanes

The procedure was identical to that described above for the 1-phenylalkanes.

The brominated hydrocarbons formed in all these reactions were only moderately stable under the analytical conditions employed. Extensive tailing was observed and very small amounts of decomposition products noted. In certain cases these decomposition products (most likely olefins) had retention times which did not interfere with the analysis of the starting hydrocarbon. At other times, however, the decomposition products eluted with starting material. Consideration of the percent of bromide decomposition under chromatographic conditions leads to the conclusion that no more than five percent error was thus introduced. Supporting this conclusion is the fact that the relative rate of reaction of 1-phenylpentane compared to 1-phenylbutane obtained by gas-liquid chromatographic analysis and by nmr analysis, to be discussed below, are in agreement within experimental error. The relative rate of reaction of 1,6-diphenylhexane relative to 1,4-diphenylbutane obtained by gas-liquid chromatographic analysis and by nmr analysis are also in agreement within experimental error.

Procedure for Kinetic Runs for the Reaction of Bromotrichloro-
methane with the 4-Methyl-1-phenyl-4-(substitutedphenyl)pentanes

Solutions of the 4-methyl-1-phenyl-4-(substitutedphenyl)pentane, diphenylmethane, and bromotrichloromethane were prepared in the approximate molar ratios of 1:2:30. Reaction times varied from three to five hours, by which time 30% to 60% of the total hydrocarbons had reacted.

Attempted analysis by gas-liquid chromatography was unsuccessful. The brominated hydrocarbons formed as products decomposed under analytical conditions and the decomposition products eluted with the starting material. The error thus introduced made analysis by gas-liquid chromatography useless.

Analysis of the mixtures, both before and after reaction, was carried out via nmr spectroscopy. Some part of the spectra that did not change during the reaction, usually the dimethyl singlet at approximately 1.15 δ , was used as an internal standard. Then the disappearance of the benzylic proton triplet of the 4-methyl-1-phenyl-4-(substitutedphenyl)pentane and the benzylic proton singlet of diphenylmethane were used to determine the relative rates.

In all other ways the procedure for the kinetic runs for these compounds were the same as that outlined above for the 1-phenylalkanes and α,ω -diphenylalkanes.

Procedure for Kinetic Runs for the Reaction of Bromotrichloro-
methane with the 4-Phenyl-1-substitutedbutanes

Solutions of 4-phenyl-1-substitutedbutanes, diphenylmethane, and bromotrichloromethane were prepared in the approximate molar ratio of 1:1:10. Analysis of the mixture both before and after reaction was carried out via nmr spectroscopy. Some part of the spectrum that did not change in integration during the reaction, usually all or part of the non-benzylic aliphatic part of the spectrum, was used as an internal standard. The disappearance of the benzylic triplet of the 4-phenyl-1-substitutedbutane and the benzylic singlet of the diphenylmethane were used to determine the relative rates of reaction. In all other ways the procedure was the same as outlined above for the 1-phenylalkanes.

Determination of Relative Rates of Hydrogen Abstraction

The ratios of the relative rate constants were obtained using the usual competitive procedures (18, 25). The relative rates of disappearance for the two materials are given by Equation 9.

$$\left[\frac{k_X}{k_S} \right]_{\text{dis.}} = \frac{\log(X_0/X_f)}{\log(S_0/S_f)} \quad (9)$$

$[k_X/k_S]_{\text{dis.}}$ is the relative rate constant for the disappearance of given compound relative to the standard compound in that series.

For the 1-phenylalkanes, the standard was 1-phenylethane. For the α,ω -diphenylalkanes the standard was 1,2-diphenylethane. For the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes and the 4-phenyl-1-substitutedbutanes the standard compound was diphenylmethane. X_0 and S_0 are the number of mmoles originally present of the given compound and the standard compound of that series respectively. X_f and S_f are the corresponding terms for the final number of mmoles present.

For the reaction of the 1-phenylalkanes and α,ω -diphenylalkanes, the ratios (X_0/X_f) or (S_0/S_f) can be obtained directly from gas-liquid chromatographic analysis using Equation 10.

$$\frac{X_0}{X_f} = \frac{\left[\frac{\text{area under X peak}}{\text{area under C}_6\text{H}_4\text{Cl}_2 \text{ peak}} \right] \text{ initially}}{\left[\frac{\text{area under X peak}}{\text{area under C}_6\text{H}_4\text{Cl}_2 \text{ peak}} \right] \text{ finally}} \quad (10)$$

For the reaction of 4-methyl-1-phenyl-4-(substitutedphenyl)-pentanes and 4-phenyl-1-substitutedbutanes the ratios (X_0/X_f) or (S_0/S_f) can be obtained directly from nmr analysis using Equation 11.

$$\frac{X_0}{X_f} = \frac{\left[\frac{\text{integration of benzylic peak}}{\text{integration of standard peak}} \right] \text{ initially}}{\left[\frac{\text{integration of benzylic peak}}{\text{integration of standard peak}} \right] \text{ finally}} \quad (11)$$

Complete detailed data on the relative rates of disappearance for each series of compounds can be found in the Appendix. The rate data for the reaction of the 1-phenylalkanes with N-bromosuccinimide or with bromotrichloromethane can be found in Appendix 1, Tables 12-19, or Appendix 2, Tables 20-27, respectively. The rate data for the reaction of the α,ω -diphenylalkanes with N-bromosuccinimide or with bromotrichloromethane can be found in Appendix 3, Tables 28-35, or Appendix 4, Tables 36-43, respectively. The rate data for the reaction of the 4-methyl-1-phenyl-4-(substitutedphenyl)pentanes with bromotrichloromethane can be found in Appendix 5, Tables 44-50. The rate data for the reaction of the 4-phenyl-1-substitutedbutanes with bromotrichloromethane can be found in Appendix 6, Tables 51-58.

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APPENDICES

APPENDIX 1

Kinetic Studies of the Reaction Between 1-Phenylalkanes
and N-Bromosuccinimide; Initiation with Light

Table 12. Relative rates of disappearance of 1-phenylpropane vs 1-phenyldecane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylpropane}}}{k_{1\text{-phenyldecane}}}\right)$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.467; Mmoles CCl_4 : 39.196						
1	1-phenylpropane	6.747	4.394	2.353	34.87	1.116
	1-phenyldecane	4.493	3.155	1.338	29.78	
	N-bromosuccinimide	3.536				
2	1-phenylpropane	6.747	3.374	3.373	49.99	1.256
	1-phenyldecane	4.493	2.509	1.984	44.16	
	N-bromosuccinimide	3.536				
3	1-phenylpropane	6.747	4.138	2.609	38.67	1.261
	1-phenyldecane	4.493	3.047	1.446	32.18	
	N-bromosuccinimide	3.536				
4	1-phenylpropane	6.747	2.240	4.507	66.80	1.085
	1-phenyldecane	4.493	1.773	2.720	60.54	
	N-bromosuccinimide	3.536				
Conditions: 2 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_5\text{Cl}$: 4.403; Mmoles CCl_4 : 38.679						
1	1-phenylpropane	7.566	4.482	3.084	40.76	1.105
	1-phenyldecane	4.586	2.856	1.730	37.72	
	N-bromosuccinimide	4.215				
2	1-phenylpropane	7.566	3.863	3.703	48.94	1.047
	1-phenyldecane	4.586	2.413	2.173	47.38	
	N-bromosuccinimide	4.215				
3	1-phenylpropane	7.566	6.121	1.445	19.10	1.007
	1-phenyldecane	4.586	3.716	0.870	18.97	
	N-bromosuccinimide	4.215				
4	1-phenylpropane	7.566	3.086	4.480	59.21	1.121
	1-phenyldecane	4.586	2.061	2.525	55.06	
	N-bromosuccinimide	4.215				
5	1-phenylpropane	7.566	4.172	3.394	44.86	1.086
	1-phenyldecane	4.586	2.651	1.935	42.19	
	N-bromosuccinimide	4.215				
Average $\left(\frac{k_{1\text{-phenylpropane}}}{k_{1\text{-phenyldecane}}}\right) = 1.120 \pm 0.056$						
Rate relative to 1-phenylethane = $(.782)(1.120) = 0.876 \pm 0.035$						

Table 13. Relative rates of disappearance of 1-phenylbutane vs phenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylbutane}}}{k_{\text{phenylethane}}} \right)$
Conditions: 2.0 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.512; Mmoles CCl_4 : 35.529						
1	1-phenylbutane	6.086	3.797	2.289	37.61	0.764
	phenylethane	4.100	2.211	1.889	46.07	
	N-bromosuccinimide	5.599				
2	1-phenylbutane	6.086	3.140	2.946	48.41	0.776
	phenylethane	4.100	1.748	2.352	57.37	
	N-bromosuccinimide	5.599				
3	1-phenylbutane	6.086	3.293	2.793	45.89	0.759
	phenylethane	4.100	1.825	2.275	55.49	
	N-bromosuccinimide	5.599				
4	1-phenylbutane	6.086	3.170	2.916	47.91	0.710
	phenylethane	4.100	1.635	2.465	60.12	
	N-bromosuccinimide	5.599				
5	1-phenylbutane	6.086	1.770	4.316	70.92	0.801
	phenylethane	4.100	0.877	3.223	78.61	
	N-bromosuccinimide	5.599				
6	1-phenylbutane	6.086	2.381	3.705	60.88	0.732
	phenylethane	4.100	1.137	2.963	72.27	
	N-bromosuccinimide	5.599				
Average $\left(\frac{k_{1\text{-phenylbutane}}}{k_{\text{phenylethane}}} \right) = 0.757 \pm 0.024$						

Table 14. Relative rates of disappearance of 1-phenylpentane vs 1-phenyldecane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1\text{-phenylpentane}}}{k_{1\text{-phenyldecane}}}$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 4.1752; Mmoles CCl_4 : 39.447						
1	1-phenylpentane	5.664	2.467	2.197	38.79	1.023
	1-phenyldecane	5.178	2.298	2.880	55.62	
	N-bromosuccinimide	4.496				
2	1-phenylpentane	5.664	2.568	3.096	54.66	1.143
	1-phenyldecane	5.178	2.592	2.586	49.94	
	N-bromosuccinimide	4.496				
3	1-phenylpentane	5.664	2.718	2.946	52.01	1.158
	1-phenyldecane	5.178	2.747	2.431	46.95	
	N-bromosuccinimide	4.496				
4	1-phenylpentane	5.664	2.699	2.965	52.35	1.058
	1-phenyldecane	5.178	2.570	2.608	50.37	
	N-bromosuccinimide	4.496				
5	1-phenylpentane	5.664	3.456	2.208	38.98	1.070
	1-phenyldecane	5.178	3.264	1.914	36.96	
	N-bromosuccinimide	4.496				
Average $(k_{1\text{-phenylpentane}}/k_{1\text{-phenyldecane}}) = 1.090 \pm 0.480$						
Rate relative to phenylethane = $(1.090)(0.782) = 0.852 \pm 0.034$						

Table 15. Relative rate of disappearance of 1-phenylhexane vs phenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylhexane}}}{k_{\text{phenylethane}}}\right)$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 4.085; Mmoles CCl_4 : 39.242						
1	1-phenylhexane	4.972	3.128	1.844	37.09	0.687
	phenylethane	6.637	3.382	3.255	49.04	
	N-bromosuccinimide	4.325				
2	1-phenylhexane	4.972	2.996	1.976	39.74	0.855
	phenylethane	6.637	3.660	2.977	44.85	
	N-bromosuccinimide	4.325				
3	1-phenylhexane	4.972	2.479	2.493	50.14	0.761
	phenylethane	6.637	2.659	3.978	59.94	
	N-bromosuccinimide	4.325				
4	1-phenylhexane	4.972	3.004	1.968	39.58	0.822
	phenylethane	6.637	3.595	3.042	45.83	
	N-bromosuccinimide	4.325				
5	1-phenylhexane	4.972	2.812	2.160	43.44	0.939
	phenylethane	6.637	3.571	3.066	46.20	
	N-bromosuccinimide	4.325				
6	1-phenylhexane	4.972	3.149	1.823	36.67	0.735
	phenylethane	6.637	3.517	3.120	47.01	
	N-bromosuccinimide	4.325				

(continued)

Table 15. Continued.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylhexane}}}{k_{\text{phenylethane}}}\right)$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.830; Mmoles CCl_4 : 39.280						
1	1-phenylhexane	5.045	3.958	1.087	21.55	0.779
	phenylethane	6.798	4.230	2.568	37.78	
	N-bromosuccinimide	4.940				
2	1-phenylhexane	5.045	3.780	1.265	25.07	0.603
	phenylethane	6.798	4.643	2.155	31.70	
	N-bromosuccinimide	4.940				
3	1-phenylhexane	5.045	3.042	2.003	39.70	0.752
	phenylethane	6.798	3.471	3.327	48.94	
	N-bromosuccinimide	4.940				
4	1-phenylhexane	5.045	2.481	2.564	19.68	0.674
	phenylethane	6.798	2.372	4.426	65.11	
	N-bromosuccinimide	4.940				
5	1-phenylhexane	5.045	2.874	2.171	43.03	0.735
	phenylethane	6.798	3.161	3.637	53.50	
	N-bromosuccinimide	4.940				
6	1-phenylhexane	5.045	3.452	1.593	31.58	0.717
	phenylethane	6.798	4.003	2.795	41.12	
	N-bromosuccinimide	4.940				
Average $\left(\frac{k_{1\text{-phenylhexane}}}{k_{\text{phenylethane}}}\right) = 0.755 \pm 0.060$						

Table 16. Relative rate of disappearance of 1-phenylheptane vs phenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylheptane}}}{k_{\text{phenylethane}}}\right)$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.563; Mmoles CCl_4 : 42.257						
1	1-phenylheptane	2.839	1.356	1.483	52.24	0.840
	phenylethane	5.140	2.133	3.007	58.50	
	N-bromosuccinimide	4.175				
2	1-phenylheptane	2.839	1.243	1.596	56.22	0.794
	phenylethane	5.140	1.816	3.324	64.67	
	N-bromosuccinimide	4.175				
3	1-phenylheptane	2.839	1.684	1.155	40.68	0.856
	phenylethane	5.140	2.792	2.348	45.68	
	N-bromosuccinimide	4.175				
4	1-phenylheptane	2.829	1.444	1.385	48.96	0.889
	phenylethane	5.140	2.404	2.736	53.23	
	N-bromosuccinimide	4.175				
5	1-phenylheptane	2.829	1.434	1.395	49.31	0.774
	phenylethane	5.140	2.128	3.012	58.60	
	N-bromosuccinimide	4.175				
Average $\left(\frac{k_{1\text{-phenylheptane}}}{k_{\text{phenylethane}}}\right) = 0.831 \pm 0.037$						

Table 17. Relative rate of disappearance of 1-phenyloctane vs phenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1\text{-phenyloctane}}}{k_{\text{phenylethane}}}$
Conditions: 1 hour 45 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.976; Mmoles CCl_4 : 37.208						
1	1-phenyloctane	6.294	4.641	1.653	26.26	0.562
	phenylethane	4.799	2.791	2.008	41.84	
	N-bromosuccinimide	4.079				
2	1-phenyloctane	6.294	4.384	1.910	30.35	0.722
	phenylethane	4.799	2.907	1.892	39.42	
	N-bromosuccinimide	4.079				
3	1-phenyloctane	6.294	4.581	1.713	27.27	0.915
	phenylethane	4.799	2.701	2.098	43.72	
	N-bromosuccinimide	4.079				
4	1-phenyloctane	6.294	4.759	1.535	24.39	0.703
	phenylethane	4.799	3.223	1.576	32.84	
	N-bromosuccinimide	4.079				
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.448; Mmoles CCl_4 : 39.043						
1	1-phenyloctane	5.106	2.635	2.471	48.39	0.725
	phenylethane	7.424	4.595	2.829	38.11	
	N-bromosuccinimide	4.215				
2	1-phenyloctane	5.106	3.230	1.876	36.74	0.759
	phenylethane	7.424	5.243	2.181	29.38	
	N-bromosuccinimide	4.215				
3	1-phenyloctane	5.106	2.229	2.877	56.35	0.766
	phenylethane	7.424	3.935	3.489	47.00	
	N-bromosuccinimide	4.215				
4	1-phenyloctane	5.106	2.939	2.167	42.44	0.720
	phenylethane	7.424	4.990	2.434	32.79	
	N-bromosuccinimide	4.215				
5	1-phenyloctane	5.106	2.341	2.765	54.15	0.804
	phenylethane	7.424	3.965	3.459	46.59	
	N-bromosuccinimide	4.215				
6	1-phenyloctane	5.106	2.822	2.284	44.73	0.767
	phenylethane	7.424	4.710	2.714	36.56	
	N-bromosuccinimide	4.215				
Average ($\frac{k_{1\text{-phenyloctane}}}{k_{\text{phenylethane}}}$) = 0.765 ± 0.039						

Table 18. Relative rate of disappearance of 1-phenylnonane vs phenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylnonane}}}{k_{\text{phenylethane}}}\right)$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.677; Mmoles CCl_4 : 37.710						
1	1-phenylnonane	5.886	4.615	1.271	21.59	0.774
	phenylethane	4.277	3.123	1.154	26.98	
	N-bromosuccinimide	4.910				
2	1-phenylnonane	5.886	3.799	2.087	35.46	0.612
	phenylethane	4.277	2.173	2.104	49.19	
	N-bromosuccinimide	4.910				
3	1-phenylnonane	5.886	4.316	1.570	26.67	0.646
	phenylethane	4.277	2.642	1.635	38.23	
	N-bromosuccinimide	4.910				
4	1-phenylnonane	5.886	3.281	2.605	44.26	0.709
	phenylethane	4.277	1.876	2.401	56.14	
	N-bromosuccinimide	4.910				
5	1-phenylnonane	5.886	2.688	3.198	54.33	0.750
	phenylethane	4.277	1.505	2.772	64.81	
	N-bromosuccinimide	4.910				
6	1-phenylnonane	5.886	4.416	1.470	24.97	0.670
	phenylethane	4.277	2.785	1.492	34.88	
	N-bromosuccinimide	4.910				
7	1-phenylnonane	5.886	3.168	2.718	46.18	0.702
	phenylethane	4.277	1.771	2.506	58.59	
	N-bromosuccinimide	4.910				
Average $\left(\frac{k_{1\text{-phenylnonane}}}{k_{\text{phenylethane}}}\right) = 0.695 \pm 0.031$						

Table 19. Relative rate of disappearance of 1-phenyldecane vs phenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1\text{-phenyldecane}}}{k_{\text{phenylethane}}}$
Conditions: 1 hours 45 minutes at 70.0°C; Mmoles C ₆ H ₄ Cl ₂ : 3.482; Mmoles CCl ₄ : 37.990						
1	1-phenyldecane	6.286	4.520	1.766	28.09	0.698
	phenylethane	6.924	4.314	2.610	37.69	
	N-bromosuccinimide	4.854				
2	1-phenyldecane	6.286	4.703	1.583	25.18	0.786
	phenylethane	6.924	4.470	2.454	35.44	
	N-bromosuccinimide	4.854				
3	1-phenyldecane	6.286	4.157	2.129	33.87	0.827
	phenylethane	6.924	4.199	2.725	39.36	
	N-bromosuccinimide	4.854				
4	1-phenyldecane	6.286	3.657	2.629	41.82	0.727
	phenylethane	6.924	3.284	3.637	52.53	
	N-bromosuccinimide	4.854				
5	1-phenyldecane	6.286	4.756	1.530	24.34	0.799
	phenylethane	6.924	4.882	2.042	29.49	
	N-bromosuccinimide	4.854				
Conditions: 2 hours at 70.0 ± 0.5°C; Mmoles C ₆ H ₄ Cl ₂ : 4.424; Mmoles CCl ₄ : 42.593						
1	1-phenyldecane	4.704	3.362	1.242	26.40	0.825
	phenylethane	7.597	5.075	2.522	33.20	
	N-bromosuccinimide	4.533				
2	1-phenyldecane	4.704	2.957	1.747	37.14	0.750
	phenylethane	7.597	4.090	3.507	46.15	
	N-bromosuccinimide	4.533				
3	1-phenyldecane	4.704	2.963	1.741	37.01	0.906
	phenylethane	7.597	4.561	3.036	39.96	
	N-bromosuccinimide	4.533				
4	1-phenyldecane	4.704	3.628	1.076	22.87	0.728
	phenylethane	7.597	5.318	2.279	30.00	
	N-bromosuccinimide	4.533				
5	1-phenyldecane	4.704	2.654	2.050	43.58	0.778
	phenylethane	7.597	3.642	3.955	52.06	
	N-bromosuccinimide	4.533				
Average ($\frac{k_{1\text{-phenyldecane}}}{k_{\text{phenylethane}}}$) = 0.782 ± 0.046						

APPENDIX 2

Kinetic Studies of the Reaction Between 1-Phenylalkanes
and Bromotrichloromethane; Initiated with Light

Table 20. Relative rates of disappearance of 1-phenylpropane vs 1-phenylnonane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylpropane}}}{k_{1\text{-phenylnonane}}}\right)$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_5\text{Cl}$: 4.152						
1	1-phenylpropane	6.015	1.182	4.833	80.35	1.087
	1-phenylnonane	5.047	1.129	3.918	77.63	
	BrCCl_3	28.52				
2	1-phenylpropane	6.015	0.802	5.213	86.67	1.280
	1-phenylnonane	5.047	1.046	4.001	79.27	
	BrCCl_3	28.52				
3	1-phenylpropane	6.015	0.927	5.088	84.59	1.318
	1-phenylnonane	5.047	1.221	3.826	75.81	
	BrCCl_3	28.52				
4	1-phenylpropane	6.015	0.832	5.185	86.17	1.256
	1-phenylnonane	5.047	1.045	4.002	70.29	
	BrCCl_3	28.52				
5	1-phenylpropane	6.015	1.075	4.940	82.13	1.172
	1-phenylnonane	5.047	1.162	3.885	76.98	
	BrCCl_3	28.52				
6	1-phenylpropane	6.015	1.105	4.910	81.63	1.194
	1-phenylnonane	5.047	1.221	3.826	75.81	
	BrCCl_3	28.52				
7	1-phenylpropane	6.015	0.911	5.104	84.85	1.240
	1-phenylnonane	5.047	1.102	3.945	78.17	
	BrCCl_3	28.52				

Average $\left(\frac{k_{1\text{-phenylpropane}}}{k_{1\text{-phenylnonane}}}\right) = 1.221 \pm 0.044$

Rate relative to 1-phenylethane = $(1.221)(0.695) = 0.849 \pm 0.031$

Table 21. Relative rates of disappearance of 1-phenylbutane vs 1-phenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylbutane}}}{k_{1\text{-phenylethane}}}\right)$
Conditions: 10.5 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 2.224						
1	1-phenylbutane	4.871	4.535	0.336	6.90	0.789
	1-phenylethane	4.468	4.029	0.439	9.83	
	BrCCl_3	22.363				
2	1-phenylbutane	4.871	0.783	4.088	83.93	0.679
	1-phenylethane	4.468	0.302	4.166	93.24	
	BrCCl_3	22.363				
3	1-phenylbutane	4.871	1.397	3.474	71.32	0.679
	1-phenylethane	4.468	0.710	3.758	84.11	
	BrCCl_3	22.363				
4	1-phenylbutane	4.871	4.595	0.276	5.67	0.786
	1-phenylethane	4.468	4.149	0.319	7.14	
	BrCCl_3	22.363				
Average $\left(\frac{k_{1\text{-phenylbutane}}}{k_{1\text{-phenylethane}}}\right) = 0.733 \pm 0.054$						

Table 22. Relative rates of disappearance of 1-phenylpentane vs 1-phenyldecane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1\text{-phenylpentane}}}{k_{1\text{-phenyldecane}}}$
Conditions: 3 hours and 20 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 2.817						
1	1-phenylpentane	6.357	3.929	2.428	38.19	0.939
	1-phenyldecane	5.452	3.267	2.185	40.08	
	BrCCl_3	29.671				
2	1-phenylpentane	6.357	3.301	3.056	48.07	0.978
	1-phenyldecane	5.452	2.790	2.662	48.83	
	BrCCl_3	29.671				
3	1-phenylpentane	6.357	3.180	3.177	49.98	0.915
	1-phenyldecane	5.452	2.557	2.895	53.10	
	BrCCl_3	29.671				
4	1-phenylpentane	6.357	3.834	2.523	39.69	0.976
	1-phenyldecane	5.452	3.247	2.205	40.44	
	BrCCl_3	29.671				
5	1-phenylpentane	6.357	3.955	2.402	37.79	0.936
	1-phenyldecane	5.452	3.284	2.168	39.77	
	BrCCl_3	29.671				

Average $(k_{1\text{-phenylpentane}}/k_{1\text{-phenyldecane}}) = 0.949 \pm 0.023$

Rate relative to 1-phenylethane = $(0.949)(0.700) = 0.664 \pm 0.016$

Table 23. Relative rates of disappearance of 1-phenylhexane vs 1-phenyldecane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylhexane}}}{k_{1\text{-phenyldecane}}}\right)$
Conditions: 4 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.962						
1	1-phenylhexane	4.746	1.929	2.817	59.36	0.962
	1-phenyldecane	4.596	1.802	2.794	60.79	
	BrCCl_3	29.150				
2	1-phenylhexane	4.746	1.492	3.254	68.56	0.998
	1-phenyldecane	4.596	1.441	3.155	68.65	
	BrCCl_3	29.150				
3	1-phenylhexane	4.746	1.292	3.454	72.78	1.022
	1-phenyldecane	4.596	1.287	3.309	72.00	
	BrCCl_3	29.150				
4	1-phenylhexane	4.746	1.144	3.602	75.90	1.018
	1-phenyldecane	4.596	1.137	3.459	75.26	
	BrCCl_3	29.150				
5	1-phenylhexane	4.746	1.410	3.336	70.29	1.043
	1-phenyldecane	4.596	1.436	3.160	68.76	
	BrCCl_3	29.150				
6	1-phenylhexane	4.746	2.185	2.561	53.96	0.938
	1-phenyldecane	4.596	2.010	2.586	56.27	
	BrCCl_3	29.150				
7	1-phenylhexane	4.746	2.282	2.464	51.92	0.971
	1-phenyldecane	4.596	2.162	2.434	52.96	
	BrCCl_3	29.150				
Average $\left(\frac{k_{1\text{-phenylhexane}}}{k_{1\text{-phenyldecane}}}\right) = 0.993 \pm 0.028$						
Rate relative to 1-phenylethane = $(0.993)(0.700) = 0.695 \pm 0.196$						

Table 24. Relative rates of disappearance of 1-phenylheptane vs phenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylheptane}}}{k_{1\text{-phenylethane}}}\right)$
Conditions: 3 hours 30 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 5.144						
1	1-phenylheptane	5.801	1.338	4.463	76.94	0.615
	1-phenylethane	4.739	0.436	4.303	90.80	
	BrCCl_3	35.828				
2	1-phenylheptane	5.801	0.864	4.937	85.11	0.652
	1-phenylethane	4.739	0.255	4.484	94.62	
	BrCCl_3	35.828				
3	1-phenylheptane	5.801	0.93	4.898	84.43	0.623
	1-phenylethane	4.739	0.239	4.500	94.96	
	BrCCl_3	35.828				
4	1-phenylheptane	5.801	0.861	4.940	85.16	0.662
	1-phenylethane	4.739	0.266	4.473	94.39	
	BrCCl_3	35.828				
5	1-phenylheptane	5.801	0.780	5.021	86.55	0.643
	1-phenylethane	4.739	0.209	4.530	95.59	
	BrCCl_3	35.828				
6	1-phenylheptane	5.801	1.027	4.774	82.30	0.645
	1-phenylethane	4.739	0.323	4.416	93.18	
	BrCCl_3	35.828				
Average $\left(\frac{k_{1\text{-phenylheptane}}}{k_{1\text{-phenylethane}}}\right) = 0.640 \pm 0.014$						

Table 25. Relative rates of disappearance of 1-phenyloctane vs phenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylnonane}}}{k_{\text{phenylethane}}}\right)$
Conditions: 4 hours 30 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.182						
1	1-phenyloctane	5.330	2.469	2.861	53.68	0.715
	phenylethane	5.025	1.712	3.313	65.93	
	BrCCl_3	26.780				
2	1-phenyloctane	5.330	2.278	3.052	57.26	0.746
	phenylethane	5.025	1.607	3.418	68.02	
	BrCCl_3	26.780				
3	1-phenyloctane	5.330	2.162	3.168	59.44	0.735
	phenylethane	5.025	1.472	3.553	70.71	
	BrCCl_3	26.780				
4	1-phenyloctane	5.330	2.329	3.001	56.30	0.763
	phenylethane	5.025	1.696	3.329	66.25	
	BrCCl_3	26.780				
5	1-phenyloctane	5.330	2.444	2.886	54.15	0.729
	phenylethane	5.025	1.723	3.302	65.71	
	BrCCl_3	26.780				
6	1-phenyloctane	5.330	1.949	3.381	63.43	0.711
	phenylethane	5.025	1.222	3.803	75.68	
	BrCCl_3	26.780				
Average $\left(\frac{k_{1\text{-phenyloctane}}}{k_{\text{phenylethane}}}\right) = 0.733 \pm 0.014$						

Table 26. Relative rates of disappearance of 1-phenylnonane vs phenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-phenylnonane}}}{k_{1\text{-phenylethane}}}\right)$
Conditions: 10 hours 30 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.465						
1	1-phenylnonane	6.225	1.457	4.768	76.59	0.679
	1-phenylethane	6.085	0.717	5.368	88.22	
	BrCCl_3	26.052				
2	1-phenylnonane	6.225	1.275	4.950	79.52	0.697
	1-phenylethane	6.085	0.625	5.460	89.73	
	BrCCl_3	26.052				
3	1-phenylnonane	6.225	1.846	4.379	70.35	0.685
	1-phenylethane	6.085	1.031	5.054	83.06	
	BrCCl_3	26.052				
4	1-phenylnonane	6.225	1.576	4.649	74.68	0.631
	1-phenylethane	6.085	0.679	5.396	88.68	
	BrCCl_3	26.052				
5	1-phenylnonane	6.225	1.357	4.868	78.20	0.683
	1-phenylethane	6.085	0.653	5.432	89.27	
	BrCCl_3	26.052				
6	1-phenylnonane	6.225	1.334	4.891	78.57	0.671
	1-phenylethane	6.085	0.612	5.473	89.94	
	BrCCl_3	26.052				
7	1-phenylnonane	6.225	1.454	4.771	76.64	0.669
	1-phenylethane	6.085	0.692	5.393	88.63	
	BrCCl_3	26.052				
Average $\left(\frac{k_{1\text{-phenylnonane}}}{k_{1\text{-phenylethane}}}\right) = 0.674 \pm 0.014$						

Table 27. Relative rates of disappearance of 1-phenyldecane vs phenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1\text{-phenyldecane}}}{k_{1\text{-phenylethane}}}$
Conditions: 14 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 2.203						
1	1-phenyldecane	8.072	2.903	5.169	64.04	0.698
	1-phenylethane	5.393	1.245	4.148	76.91	
	BrCCl_3	25.713				
2	1-phenyldecane	8.072	3.279	4.793	59.38	0.758
	1-phenylethane	5.393	1.643	3.750	69.53	
	BrCCl_3	25.713				
3	1-phenyldecane	8.072	6.401	1.671	20.70	0.771
	1-phenylethane	5.393	3.992	1.401	25.98	
	BrCCl_3	25.713				
4	1-phenyldecane	8.072	7.305	0.767	9.50	0.661
	1-phenylethane	5.393	4.637	0.756	14.02	
	BrCCl_3	25.713				
5	1-phenyldecane	8.072	2.779	5.293	65.57	0.657
	1-phenylethane	5.393	1.063	4.330	80.29	
	BrCCl_3	25.713				
6	1-phenyldecane	8.072	2.773	5.299	65.65	0.656
	1-phenylethane	5.393	1.058	4.335	80.38	
	BrCCl_3	25.713				
Average $(\frac{k_{1\text{-phenyldecane}}}{k_{1\text{-phenylethane}}}) = 0.700 \pm 0.043$						

APPENDIX 3

Kinetic Studies of the Reaction Between α,ω -Diphenylalkanes
and N-Bromosuccinimide; Initiated with Light

Table 28. Relative rates of disappearance of 1,3-diphenylpropane vs 1,2-diphenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,3\text{-diphenylpropane}}}{k_{1,2\text{-diphenylethane}}}$
Conditions: 2 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 2.542; Mmoles CCl_4 : 35.086						
1	1,3-diphenylpropane	3.433	1.300	2.133	62.13	1.428
	1,2-diphenylethane	2.518	1.276	1.242	49.32	
	N-bromosuccinimide	3.971				
2	1,3-diphenylpropane	3.433	0.555	2.878	83.83	1.364
	1,2-diphenylethane	2.518	0.662	1.856	73.71	
	N-bromosuccinimide	3.971				
3	1,3-diphenylpropane	3.433	1.756	1.677	48.85	1.611
	1,2-diphenylethane	2.513	1.661	0.857	34.03	
	N-bromosuccinimide	3.971				
4	1,3-diphenylpropane	3.433	1.770	1.663	48.44	1.532
	1,2-diphenylethane	2.518	1.634	0.884	35.11	
	N-bromosuccinimide	3.971				
5	1,3-diphenylpropane	3.433	1.142	2.291	66.73	1.474
	1,2-diphenylethane	2.518	1.193	1.325	52.62	
	N-bromosuccinimide	3.971				
6	1,3-diphenylpropane	3.433	1.180	2.253	65.63	1.483
	1,2-diphenylethane	2.518	1.225	1.293	51.35	
	N-bromosuccinimide	3.971				
Average ($k_{1,3\text{-diphenylpropane}}/k_{1,2\text{-diphenylethane}}$) = 1.482 ± 0.060						

Table 29. Relative rates of disappearance of 1,4-diphenylbutane vs 1,10-diphenyldecane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,4\text{-diphenylbutane}}}{k_{1,10\text{-diphenyldecane}}}\right)$
Conditions: 1 hours 10 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.388; Mmoles CCl_4 : 38.539						
1	1,4-diphenylbutane	3.672	2.235	1.437	39.13	1.015
	1,10-diphenyldecane	4.640	2.868	1.772	38.20	
	N-bromosuccinimide	4.781				
2	1,4-diphenylbutane	3.672	2.231	1.441	39.25	1.135
	1,10-diphenyldecane	4.640	2.991	1.649	35.55	
	N-bromosuccinimide	4.781				
3	1,4-diphenylbutane	3.672	1.776	1.896	51.62	1.042
	1,10-diphenyldecane	4.640	2.310	2.330	50.21	
	N-bromosuccinimide	4.781				
4	1,4-diphenylbutane	3.672	1.787	1.885	51.34	1.001
	1,10-diphenyldecane	4.640	2.261	2.379	51.27	
	N-bromosuccinimide	4.781				
5	1,4-diphenylbutane	3.672	2.643	1.029	28.03	0.9005
	1,10-diphenyldecane	4.640	3.228	1.412	30.44	
	N-bromosuccinimide	4.781				
6	1,4-diphenylbutane	3.672	1.796	1.876	51.09	1.006
	1,10-diphenyldecane	4.640	2.279	1.361	50.87	
	N-bromosuccinimide	4.781				

(continued)

Table 29. Continued.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,4\text{-diphenylbutane}}}{k_{1,10\text{-diphenyldecane}}}\right)$
Conditions: 70 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 6.204; Mmoles CCl_4 : 41.049						
1	1, 4-diphenylbutane	3.119	2.192	0.927	29.72	0.971
	1, 10-diphenyldecane	5.592	3.889	1.703	30.45	
	N-bromosuccinimide	6.942				
2	1, 4-diphenylbutane	3.119	2.234	.885	28.37	0.915
	1, 10-diphenyldecane	5.592	3.883	1.709	30.56	
	N-bromosuccinimide	6.942				
3	1, 4-diphenylbutane	3.119	1.779	1.340	42.96	1.010
	1, 10-diphenyldecane	5.592	3.208	2.384	42.63	
	N-bromosuccinimide	6.942				
4	1, 4-diphenylbutane	3.119	2.217	0.902	28.92	1.030
	1, 10-diphenyldecane	5.592	4.014	1.578	28.22	
	N-bromosuccinimide	6.942				
5	1, 4-diphenylbutane	3.119	1.520	1.599	51.27	1.138
	1, 10-diphenyldecane	5.592	2.973	2.619	46.83	
	N-bromosuccinimide	6.942				
6	1, 4-diphenylbutane	3.119	1.185	1.934	62.01	1.017
	1, 10-diphenyldecane	5.592	2.159	3.433	61.29	
	N-bromosuccinimide	6.942				
Average $(k_{1,4\text{-diphenylbutane}}/k_{1,10\text{-diphenyldecane}}) = 1.015 \pm 0.031$						
Rate relative to 1, 2-diphenylbutane = $(1.015 \pm 0.031)(1.614) = 1.638 \pm 0.050$						

Table 30. Relative rates of disappearance of 1,5-diphenylpentane vs 1,2-diphenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,5\text{-diphenylpentane}}}{k_{1,2\text{-diphenylethane}}}$
Conditions: 1 hour at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 4.740; Mmoles CCl_4 : 33.755						
1	1,5-diphenylpentane	3.522	1.464	2.058	58.43	1.342
	1,2-diphenylethane	3.603	1.873	1.730	48.02	
	N-bromosuccinimide	5.607				
2	1,5-diphenylpentane	3.522	1.709	1.813	51.48	1.416
	1,2-diphenylethane	3.603	2.150	1.453	40.33	
	N-bromosuccinimide					
3	1,5-diphenylpentane	3.522	1.633	1.889	53.63	1.400
	1,2-diphenylethane	3.603	2.068	1.535	42.60	
	N-bromosuccinimide	5.607				
4	1,5-diphenylpentane	3.522	1.534	1.988	56.45	1.338
	1,2-diphenylethane	3.603	1.924	1.679	46.60	
	N-bromosuccinimide	5.607				
5	1,5-diphenylpentane	3.522	1.615	1.907	54.15	1.229
	1,2-diphenylethane	3.603	1.963	1.640	45.52	
	N-bromosuccinimide	5.607				
6	1,5-diphenylpentane	3.522	1.872	1.650	46.85	1.430
	1,2-diphenylethane	3.603	2.302	1.301	36.11	
	N-bromosuccinimide	5.607				
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.1950; Mmoles CCl_4 : 38.8253						
1	1,5-diphenylpentane	4.189	2.306	1.883	44.95	1.288
	1,2-diphenylethane	3.179	1.999	1.180	37.12	
	N-bromosuccinimide	4.214				
2	1,5-diphenylpentane	4.189	1.495	2.694	64.31	1.347
	1,2-diphenylethane	3.179	1.417	1.762	55.43	
	N-bromosuccinimide	4.214				
3	1,5-diphenylpentane	4.189	1.477	2.712	64.74	1.256
	1,2-diphenylethane	3.179	2.044	1.135	35.70	
	N-bromosuccinimide	4.214				
4	1,5-diphenylpentane	4.189	2.937	1.252	29.89	1.551
	1,2-diphenylethane	3.179	2.529	.650	20.45	
	N-bromosuccinimide	4.214				
5	1,5-diphenylpentane	4.189	1.805	2.384	56.91	1.293
	1,2-diphenylethane	3.179	1.658	1.521	47.85	
	N-bromosuccinimide	4.214				
Average $\left(\frac{k_{1,5\text{-diphenylpentane}}}{k_{1,2\text{-diphenylethane}}}\right) = 1.353 \pm 0.061$						

Table 31. Relative rates of disappearance of 1,6-diphenylhexane vs 1,2-diphenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,6\text{-diphenylhexane}}}{k_{1,2\text{-diphenylethane}}}\right)$
Conditions: 1 hour at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 4.164; Mmoles CCl_4 : 35.622						
1	1,6-diphenylhexane	4.035	2.993	1.042	25.82	1.477
	1,2-diphenylethane	3.367	2.751	0.616	18.30	
	N-bromosuccinimide	5.905				
2	1,6-diphenylhexane	4.035	2.892	1.143	28.33	1.384
	1,2-diphenylethane	3.367	2.645	0.722	21.44	
	N-bromosuccinimide	5.905				
3	1,6-diphenylhexane	4.035	3.018	1.017	25.20	1.679
	1,2-diphenylethane	3.367	2.832	0.535	15.89	
	N-bromosuccinimide	5.905				
4	1,6-diphenylhexane	4.035	1.326	2.709	67.14	1.524
	1,2-diphenylethane	3.367	1.622	1.745	51.83	
	N-bromosuccinimide	5.905				
Conditions: 3 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.770; Mmoles CCl_4 : 32.625						
1	1,6-diphenylhexane	3.720	1.686	2.034	54.68	1.521
	1,2-diphenylethane	2.434	1.519	0.915	37.59	
	N-bromosuccinimide	6.364				
2	1,6-diphenylhexane	3.720	1.455	2.265	60.89	1.533
	1,2-diphenylethane	2.434	1.320	1.114	45.77	
	N-bromosuccinimide	6.364				
3	1,6-diphenylhexane	3.720	1.584	2.136	57.42	1.631
	1,2-diphenylethane	2.434	1.442	.992	40.76	
	N-bromosuccinimide	6.364				
4	1,6-diphenylhexane	3.720	1.598	2.122	57.04	1.631
	1,2-diphenylethane	2.434	1.541	.893	36.69	
	N-bromosuccinimide	6.364				
5	1,6-diphenylhexane	3.720	1.386	2.334	62.74	1.547
	1,2-diphenylethane	2.434	1.286	1.148	47.17	
	N-bromosuccinimide	6.364				
Average $\left(\frac{k_{1,6\text{-diphenylhexane}}}{k_{1,2\text{-diphenylethane}}}\right) = 1.547 \pm 0.066$						

Table 32. Relative rates of disappearance of 1,7-diphenylheptane vs 1,2-diphenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,7\text{-diphenylheptane}}}{k_{1,2\text{-diphenylethane}}}$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.8433; Mmoles CCl_4 : 38.8961						
1	1,7-diphenylheptane	3.816	1.338	2.478	64.95	1.393
	1,2-diphenylethane	3.995	1.894	2.101	52.60	
	N-bromosuccinimide	4.168				
2	1,7-diphenylheptane	3.816	1.896	1.920	50.31	1.570
	1,2-diphenylethane	3.995	2.578	1.417	35.47	
	N-bromosuccinimide	4.168				
3	1,7-diphenylheptane	3.816	2.192	1.624	42.56	1.595
	1,2-diphenylethane	3.995	2.842	1.153	28.85	
	N-bromosuccinimide	4.168				
4	1,7-diphenylheptane	3.816	1.959	1.857	48.66	1.320
	1,2-diphenylethane	3.995	2.424	1.571	39.33	
	N-bromosuccinimide	4.168				
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.612; Mmoles CCl_4 : 38.942						
1	1,7-diphenylheptane	4.877	2.167	2.710	55.57	1.557
	1,2-diphenylethane	5.190	3.015	2.175	41.92	
	N-bromosuccinimide	3.957				
2	1,7-diphenylheptane	4.877	2.638	2.239	45.91	1.326
	1,2-diphenylethane	5.190	3.350	1.840	35.46	
	N-bromosuccinimide	3.957				
3	1,7-diphenylheptane	4.877	2.091	2.786	57.12	1.495
	1,2-diphenylethane	5.190	3.010	2.180	43.00	
	N-bromosuccinimide	3.957				
4	1,7-diphenylheptane	4.877	2.866	2.011	41.24	1.388
	1,2-diphenylethane	5.190	3.624	1.566	30.19	
	N-bromosuccinimide	3.957				
5	1,7-diphenylheptane	4.877	2.365	2.512	51.51	1.420
	1,2-diphenylethane	5.190	3.191	1.999	38.52	
	N-bromosuccinimide	3.957				
6	1,7-diphenylheptane	4.877	3.032	1.845	37.83	1.408
	1,2-diphenylethane	5.190	3.793	1.397	26.92	
	N-bromosuccinimide	3.957				
7	1,7-diphenylheptane	4.877	3.321	1.556	31.90	1.533
	1,2-diphenylethane	5.190	4.125	1.065	20.52	
	N-bromosuccinimide	3.957				
Average $(\frac{k_{1,7\text{-diphenylheptane}}}{k_{1,2\text{-diphenylethane}}}) = 1.455 \pm 0.087$						

Table 33. Relative rates of disappearance of 1,8-diphenyloctane vs 1,2-diphenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,8\text{-diphenyloctane}}}{k_{1,2\text{-diphenylethane}}}\right)$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.301; Mmoles CCl_4 : 33.007						
1	1,8-diphenyloctane	4.039	1.896	2.143	53.07	1.443
	1,2-diphenylethane	2.348	1.390	0.958	40.78	
	N-bromosuccinimide	4.024				
2	1,8-diphenyloctane	4.039	2.107	1.932	47.84	1.648
	1,2-diphenylethane	2.348	1.583	0.765	32.59	
	N-bromosuccinimide	4.024				
3	1,8-diphenyloctane	4.039	0.731	3.308	81.90	1.403
	1,2-diphenylethane	2.348	0.695	1.653	70.41	
	N-bromosuccinimide	4.024				
4	1,8-diphenyloctane	4.039	2.057	1.982	49.07	1.513
	1,2-diphenylethane	2.348	1.505	0.843	35.90	
	N-bromosuccinimide	4.024				
Conditions: 30 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.0127; Mmoles CCl_4 : 33.4930						
1	1,8-diphenyloctane	5.141	2.632	2.509	48.79	1.260
	1,2-diphenylethane	2.813	1.654	1.159	41.21	
	N-bromosuccinimide	4.168				
2	1,8-diphenyloctane	5.141	3.093	2.048	30.84	1.287
	1,2-diphenylethane	2.813	1.701	1.112	39.54	
	N-bromosuccinimide	4.168				
3	1,8-diphenyloctane	5.141	3.697	1.444	28.10	1.337
	1,2-diphenylethane	2.813	2.197	0.616	21.90	
	N-bromosuccinimide	4.168				
4	1,8-diphenyloctane	5.141	3.229	1.912	37.19	1.216
	1,2-diphenylethane	2.813	1.919	0.894	31.77	
	N-bromosuccinimide	4.168				
5	1,8-diphenyloctane	5.141	3.449	1.692	32.90	1.163
	1,2-diphenylethane	2.813	1.997	0.816	29.02	
	N-bromosuccinimide	4.168				
6	1,8-diphenyloctane	5.141	3.282	1.859	36.15	1.185
	1,2-diphenylethane	2.813	1.927	0.886	31.51	
	N-bromosuccinimide	4.168				
Average $\left(\frac{k_{1,8\text{-diphenyloctane}}}{k_{1,2\text{-diphenylethane}}}\right) = 1.346 \pm 0.126$						

Table 34. Relative rate of disappearance of 1, 9-diphenylnonane vs 1, 2-diphenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,9\text{-diphenylnonane}}}{k_{1,2\text{-diphenylethane}}}$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.765; Mmoles CCl_4 : 35.083						
1	1, 9-diphenylnonane	8.217	6.038	2.179	26.52	1.438
	1, 2-diphenylethane	2.659	2.146	0.513	19.28	
	N-bromosuccinimide	4.414				
2	1, 9-diphenylnonane	8.217	5.714	2.503	30.46	1.385
	1, 2-diphenylethane	2.659	2.045	0.614	23.09	
	N-bromosuccinimide	4.414				
3	1, 9-diphenylnonane	8.217	6.121	2.096	25.51	1.403
	1, 2-diphenylethane	2.659	2.155	0.504	18.95	
	N-bromosuccinimide	4.414				
4	1, 9-diphenylnonane	8.217	5.359	2.858	34.78	1.318
	1, 2-diphenylethane	2.659	1.923	0.736	27.69	
	N-bromosuccinimide	4.414				
5	1, 9-diphenylnonane	8.217	5.667	2.550	31.03	1.328
	1, 2-diphenylethane	2.659	1.997	0.662	24.90	
	N-bromosuccinimide	4.414				
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.200; Mmoles CCl_4 : 34.748						
1	1, 9-diphenylnonane	5.036	2.740	2.296	45.59	1.198
	1, 2-diphenylethane	2.998	1.804	1.194	39.82	
	N-bromosuccinimide	4.213				
2	1, 9-diphenylnonane	5.036	3.779	1.257	24.97	1.482
	1, 2-diphenylethane	2.998	2.465	0.533	17.76	
	N-bromosuccinimide	4.213				
3	1, 9-diphenylnonane	5.036	3.308	1.728	34.32	1.315
	1, 2-diphenylethane	2.998	2.177	0.821	27.38	
	N-bromosuccinimide	4.213				
4	1, 9-diphenylnonane	5.036	2.762	2.274	45.15	1.264
	1, 2-diphenylethane	2.998	1.119	1.879	62.68	
	N-bromosuccinimide	4.213				
5	1, 9-diphenylnonane	5.036	3.357	1.679	33.34	1.481
	1, 2-diphenylethane	2.998	2.279	0.719	23.98	
	N-bromosuccinimide	4.213				
Average $\left(\frac{k_{1,9\text{-diphenylnonane}}}{k_{1,2\text{-diphenylethane}}}\right) = 1.361 \pm 0.077$						

Table 35. Relative rates of disappearance of 1, 10-diphenyldecane vs 1, 2-diphenylethane; light initiation of N-bromosuccinimide.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1, 10\text{-diphenyldecane}}}{k_{1, 2\text{-diphenylethane}}}\right)$
Conditions: 2 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.527; Mmoles CCl_4 : 35.357						
1	1, 10-diphenyldecane	3.465	1.810	1.655	47.76	1.575
	1, 2-diphenylethane	2.932	1.942	0.990	33.77	
	N-bromosuccinimide	4.385				
2	1, 10-diphenyldecane	3.465	1.510	1.955	56.42	1.535
	1, 2-diphenylethane	2.932	1.732	1.200	40.93	
	N-bromosuccinimide	4.385				
3	1, 10-diphenyldecane	3.465	1.578	1.887	54.46	1.715
	1, 2-diphenylethane	2.932	1.853	1.079	36.80	
	N-bromosuccinimide	4.385				
4	1, 10-diphenyldecane	3.465	1.861	1.604	46.29	1.602
	1, 2-diphenylethane	2.932	1.989	0.943	32.16	
	N-bromosuccinimide	4.385				
5	1, 10-diphenyldecane	3.465	1.863	1.602	46.23	1.722
	1, 2-diphenylethane	2.932	2.045	0.887	30.25	
	N-bromosuccinimide	4.385				
6	1, 10-diphenyldecane	3.465	1.338	2.127	61.39	1.521
	1, 2-diphenylethane	2.932	1.569	1.363	46.49	
	N-bromosuccinimide	4.385				
7	1, 10-diphenyldecane	3.465	1.235	2.230	64.36	1.630
	1, 2-diphenylethane	2.932	1.557	1.375	46.90	
	N-bromosuccinimide	4.385				
Average $\left(\frac{k_{1, 10\text{-diphenyldecane}}}{k_{1, 2\text{-diphenylethane}}}\right) = 1.614 \pm 0.064$						

APPENDIX 4

Kinetic Studies of the Reaction Between α,ω -Diphenylalkanes
and Bromotrichloromethane; Initiated with Light

Table 36. Relative rates of disappearance of 1,3-diphenylpropane vs 1,2-diphenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,3\text{-diphenylpropane}}}{k_{1,2\text{-diphenylethane}}}$
Conditions: 12 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 1.554						
1	1,3-diphenylpropane	2.634	1.139	1.495	56.76	2.120
	1,2-diphenylethane	2.200	1.481	0.719	32.68	
	BrCCl_3	25.232				
2	1,3-diphenylpropane	2.634	1.136	1.498	56.87	2.127
	1,2-diphenylethane	2.200	1.481	0.719	32.68	
	BrCCl_3	25.232				
3	1,3-diphenylpropane	2.632	1.923	0.711	26.99	2.005
	1,2-diphenylethane	2.200	1.880	0.320	14.55	
	BrCCl_3	25.232				
4	1,3-diphenylpropane	2.634	2.329	0.305	11.58	1.795
	1,2-diphenylethane	2.200	2.054	0.146	6.64	
	BrCCl_3	25.232				
Average $(k_{1,3\text{-diphenylpropane}}/k_{1,2\text{-diphenylethane}}) = 2.012 \pm 0.112$						

Table 37. Relative rates of disappearance of 1,4-diphenylbutane vs 1,8-diphenyloctane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,4\text{-diphenylbutane}}}{k_{1,8\text{-diphenyloctane}}}$
Conditions: 3 hours 30 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.556						
1	1,4-diphenylbutane	3.502	1.491	2.011	57.44	0.812
	1,8-diphenyloctane	3.738	1.306	2.432	65.06	
	BrCCl_3	30.108				
2	1,4-diphenylbutane	3.502	1.074	2.428	69.34	1.023
	1,8-diphenyloctane	3.738	1.177	2.561	68.52	
	BrCCl_3	30.108				
3	1,4-diphenylbutane	3.502	1.428	2.074	59.23	0.884
	1,8-diphenyloctane	3.738	1.335	2.403	64.29	
	BrCCl_3	30.108				
4	1,4-diphenylbutane	3.502	1.382	2.120	60.53	0.934
	1,8-diphenyloctane	3.738	1.383	2.355	63.01	
	BrCCl_3	30.108				
5	1,4-diphenylbutane	3.502	1.282	2.220	63.39	0.960
	1,8-diphenyloctane	3.738	1.312	2.426	64.90	
	BrCCl_3	30.108				
Average $(k_{1,4\text{-diphenylbutane}}/k_{1,8\text{-diphenyloctane}}) = 0.923 \pm 0.058$						
Rate relative to 1,2-diphenylbutane = $(0.932)(2.595) = 2.418 \pm 0.151$						

Table 38. Relative rates of disappearance of 1,5-diphenylpentane vs diphenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,5\text{-diphenylpentane}}}{k_{1,2\text{-diphenylethane}}}\right)$
Conditions: 3 hours 20 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.870						
1	1,5-diphenylpentane	5.074	2.418	2.656	52.34	2.768
	1,2-diphenylethane	4.171	3.190	0.981	23.52	
	BrCCl_3	30.703				
2	1,5-diphenylpentane	5.074	2.824	2.250	44.36	2.136
	1,2-diphenylethane	4.171	3.217	0.954	22.88	
	BrCCl_3	30.703				
3	1,5-diphenylpentane	5.074	1.921	3.153	62.14	2.464
	1,2-diphenylethane	4.171	2.710	1.461	35.03	
	BrCCl_3	30.703				
4	1,5-diphenylpentane	5.074	2.400	2.674	52.70	2.174
	1,2-diphenylethane	4.171	2.956	1.215	29.13	
	BrCCl_3	30.703				
5	1,5-diphenylpentane	5.074	3.424	1.650	32.52	2.832
	1,2-diphenylethane	4.171	3.630	0.541	12.97	
	BrCCl_3	30.703				
6	1,5-diphenylpentane	5.074	2.413	2.661	52.44	2.738
	1,2-diphenylethane	4.171	3.179	0.992	23.78	
	BrCCl_3	30.703				

(continued)

Table 38. Continued.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,5\text{-diphenylpentane}}}{k_{1,2\text{-diphenylethane}}}$
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.564						
1	1,5-diphenylpentane	4.629	2.954	1.675	36.18	2.222
	1,2-diphenylethane	4.357	3.559	0.798	18.32	
	BrCCl_3	30.163				
2	1,5-diphenylpentane	4.629	2.528	2.101	45.39	2.980
	1,2-diphenylethane	4.357	3.557	0.800	18.36	
	BrCCl_3	30.163				
3	1,5-diphenylpentane	4.629	2.506	2.123	45.86	2.821
	1,2-diphenylethane	4.357	3.505	0.852	19.55	
	BrCCl_3	30.163				
4	1,5-diphenylpentane	4.629	1.904	2.725	58.87	2.298
	1,2-diphenylethane	4.357	2.960	1.397	32.06	
	BrCCl_3	30.163				
5	1,5-diphenylpentane	4.629	2.376	2.253	48.67	3.065
	1,2-diphenylethane	4.357	3.505	0.852	19.55	
	BrCCl_3	30.163				
6	1,5-diphenylpentane	4.629	2.165	1.464	31.63	2.651
	1,2-diphenylethane	4.357	3.271	1.086	24.93	
	BrCCl_3	30.163				

(continued)

Table 38. Continued.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,5\text{-diphenylpentane}}}{k_{1,2\text{-diphenylethane}}}$
Conditions: 4 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.675						
1	1,5-diphenylpentane	5.598	2.899	2.699	48.21	2.457
	1,2-diphenylethane	4.694	3.592	1.102	23.48	
	BrCCl_3	30.256				
2	1,5-diphenylpentane	5.598	3.063	2.535	45.28	2.383
	1,2-diphenylethane	4.694	3.645	1.049	22.35	
	BrCCl_3	30.256				
3	1,5-diphenylpentane	5.598	2.593	3.005	53.68	2.597
	1,2-diphenylethane	4.694	3.490	1.204	25.65	
	BrCCl_3	30.256				
4	1,5-diphenylpentane	5.598	2.497	3.101	55.39	2.181
	1,2-diphenylethane	4.694	3.242	1.452	30.93	
	BrCCl_3	30.256				
Conditions: 5 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.538						
1	1,5-diphenylpentane	4.604	2.287	2.317	50.317	2.367
	1,2-diphenylethane	2.902	2.159	0.743	25.603	
	BrCCl_3	28.151				
2	1,5-diphenylpentane	4.604	2.371	2.233	48.50	2.814
	1,2-diphenylethane	2.902	2.292	0.610	26.61	
	BrCCl_3	28.151				
3	1,5-diphenylpentane	4.604	2.447	2.157	46.86	2.221
	1,2-diphenylethane	2.902	2.181	0.721	24.84	
	BrCCl_3	28.151				
4	1,5-diphenylpentane	4.604	1.546	3.058	66.43	2.586
	1,2-diphenylethane	2.902	1.903	0.999	34.42	
	BrCCl_3	28.151				
5	1,5-diphenylpentane	4.604	1.660	2.944	63.95	2.200
	1,2-diphenylethane	2.902	1.825	1.077	37.11	
	BrCCl_3	28.151				
6	1,5-diphenylpentane	4.604	1.609	2.995	65.05	2.261
	1,2-diphenylethane	2.902	1.823	1.079	37.18	
	BrCCl_3	28.151				
Average $(k_{1,5\text{-diphenylpentane}}/k_{1,2\text{-diphenylethane}}) = 2.509 \pm 0.251$						

Table 39. Relative rates of disappearance of 1,6-diphenylhexane vs 1,2-diphenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,6\text{-diphenyl}}}{k_{1,2\text{-diphenyl}}}\right)$
Conditions: 8 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 2.589						
1	1,2-diphenylethane	2.425	2.012	0.413	17.0	2.886
	1,6-diphenylhexane	3.729	2.183	1.546	41.5	
	BrCCl_3	25.658				
2	1,2-diphenylethane	2.425	1.867	0.558	23.0	2.827
	1,6-diphenylhexane	3.729	1.785	0.944	52.1	
	BrCCl_3	25.658				
3	1,2-diphenylethane	2.425	2.175	0.250	10.3	3.407
	1,6-diphenylhexane	3.729	2.580	1.149	30.8	
	BrCCl_3	25.658				
4	1,2-diphenylethane	2.425	2.100	0.325	13.4	3.037
	1,6-diphenylhexane	3.729	2.414	1.315	35.3	
	BrCCl_3	25.658				
5	1,2-diphenylethane	2.425	1.874	0.551	22.7	3.523
	1,6-diphenylhexane	3.729	1.508	2.221	59.6	
	BrCCl_3	25.658				
6	1,2-diphenylethane	2.425	1.715	0.710	29.3	2.761
	1,6-diphenylhexane	3.729	1.440	2.289	61.4	
	BrCCl_3	25.658				

(continued)

Table 39. Continued.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% yr	$\frac{k_{1,6\text{-diphenyl}}}{k_{1,2\text{-diphenyl}}}$
Conditions: 5 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_3\text{Cl}_2$: 2.680						
1	1,2-diphenylethane	2.807	2.123	0.684	24.4	2.831
	1,6-diphenylhexane	5.506	2.498	3.008	54.6	
	BrCCl_3	29.049				
2	1,2-diphenylethane	2.807	2.262	0.545	19.4	3.524
	1,6-diphenylhexane	5.506	2.573	2.933	53.3	
	BrCCl_3	29.049				
3	1,2-diphenylethane	2.807	2.266	0.541	19.3	3.533
	1,6-diphenylhexane	5.506	2.583	2.923	53.1	
	BrCCl_3	29.049				
4	1,2-diphenylethane	2.807	2.339	0.468	16.7	3.104
	1,6-diphenylhexane	5.506	3.127	2.379	43.2	
	BrCCl_3	29.049				
5	1,2-diphenylethane	2.807	2.482	0.325	11.6	3.277
	1,6-diphenylhexane	5.506	3.301	2.205	40.0	
	BrCCl_3	29.049				
6	1,2-diphenylethane	2.807	2.215	0.592	21.1	3.345
	1,6-diphenylhexane	5.506	2.495	3.011	54.7	
	BrCCl_3	29.049				
Average $(k_{1,6\text{-diphenyl}}/k_{1,2\text{-diphenyl}}) = 3.171 \pm 0.220$						

Table 40. Relative rates of disappearance of 1,7-diphenylheptane vs 1,2-diphenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,7\text{-diphenyl}}}{k_{1,2\text{-diphenyl}}}$
Conditions: 3 hours 50 minutes at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.3712						
1	1,2-diphenylethane	2.712	1.798	0.913	33.7	2.762
	1,7-diphenylhexane	2.440	0.786	1.654	67.8	
	BrCCl_3	25.36				
2	1,2-diphenylethane	2.712	1.696	1.016	37.5	3.052
	1,7-diphenylhexane	2.440	0.582	1.858	76.1	
	BrCCl_3	25.36				
3	1,2-diphenylethane	2.712	1.581	1.313	41.7	2.775
	1,7-diphenylhexane	2.440	0.545	1.895	77.7	
	BrCCl_3	25.36				
4	1,2-diphenylethane	2.712	2.108	0.604	22.3	2.866
	1,7-diphenylhexane	2.440	0.182	1.258	51.6	
	BrCCl_3	25.36				
Conditions: $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.449						
1	1,2-diphenylethane	3.377	3.179	0.198	5.86	2.980
	1,7-diphenylheptane	1.988	1.661	0.327	16.4	
	BrCCl_3	2.788				
2	1,2-diphenylethane	3.377	2.881	0.496	14.7	2.918
	1,7-diphenylheptane	1.988	1.223	0.765	38.5	
	BrCCl_3	2.788				
3	1,2-diphenylethane	3.377	2.766	0.611	18.1	2.955
	1,7-diphenylheptane	1.988	1.102	0.886	44.6	
	BrCCl_3	2.788				
Average $(k_{1,7\text{-diphenylheptane}}/k_{1,2\text{-diphenylethane}}) = 2.902 \pm .087$						

Table 41. Relative rates of disappearance of 1,8-diphenyloctane vs 1,2-diphenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,8\text{-diphenyloctane}}}{k_{1,2\text{-diphenylethane}}}\right)$
Conditions: 4 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$:						
1	1,2-diphenylethane	2.9967	2.4435	0.5532	18.4603	2.490
	1,8-diphenyloctane	5.3556	3.2243	2.1313	39.7957	
	BrCCl_3	27.426				
2	1,2-diphenylethane	2.9967	2.7242	0.2725	9.0933	2.500
	1,8-diphenyloctane	5.3556	4.2208	1.1348	21.1890	
	BrCCl_3	27.426				
3	1,2-diphenylethane	2.9967	2.6328	0.3641	12.1500	2.767
	1,8-diphenyloctane	5.3556	3.7448	1.6108	30.0769	
	BrCCl_3	27.426				
4	1,2-diphenylethane	2.9967	2.4717	0.5250	17.5193	2.326
	1,8-diphenyloctane	5.3556	3.4251	1.9305	36.0464	
	BrCCl_3	27.426				
5	1,2-diphenylethane	2.9967	2.4364	0.5603	18.6972	2.563
	1,8-diphenyloctane	5.3556	3.1499	2.2057	41.1849	
	BrCCl_3	27.426				
6	1,2-diphenylethane	2.9967	2.6485	0.3482	11.6194	2.860
	1,8-diphenyloctane	5.3556	3.7667	1.5889	29.6680	
	BrCCl_3	27.426				
7	1,2-diphenylethane	2.9967	2.3049	0.6918	23.0854	2.657
	1,8-diphenyloctane	5.3556	2.6668	2.6888	50.2054	
	BrCCl_3	27.426				
Average $\left(\frac{k_{1,8\text{-diphenyloctane}}}{k_{1,2\text{-diphenylethane}}}\right) = 2.595 \pm 0.143$						

Table 42. Relative rates of disappearance of 1,9-diphenylnonane vs 1,2-diphenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1,9\text{-diphenylnonane}}}{k_{1,2\text{-diphenylethane}}}$
Conditions: 14 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 3.618						
1	1,9-diphenylnonane	5.247	3.745	1.502	28.63	2.340
	1,2-diphenylethane	2.857	2.474	0.383	13.41	
	BrCCl_3	29.335				
2	1,9-diphenylnonane	5.247	4.607	0.640	12.20	1.950
	1,2-diphenylethane	2.857	2.673	0.184	6.44	
	BrCCl_3	29.335				
3	1,9-diphenylnonane	5.247	3.966	1.281	24.41	2.165
	1,2-diphenylethane	2.857	2.511	0.346	12.11	
	BrCCl_3	29.335				
4	1,9-diphenylnonane	5.247	4.413	0.834	15.89	2.222
	1,2-diphenylethane	2.857	2.643	0.214	7.49	
	BrCCl_3	29.335				
5	1,9-diphenylnonane	5.247	4.315	0.932	17.76	2.269
	1,2-diphenylethane	2.857	2.621	0.236	8.26	
	BrCCl_3	29.335				
6	1,9-diphenylnonane	5.247	4.685	0.562	10.71	2.045
	1,2-diphenylethane	2.857	2.703	0.154	5.39	
	BrCCl_3	29.335				
7	1,9-diphenylnonane	5.247	4.881	0.366	6.98	2.296
	1,2-diphenylethane	2.857	2.768	0.089	3.12	
	BrCCl_3	29.335				
Average $(k_{1,9\text{-diphenylnonane}}/k_{1,2\text{-diphenylethane}}) = 2.180 \pm 0.110$						

Table 43. Relative rates of disappearance of 1,10-diphenyldecane vs 1,2-diphenylethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,10\text{-diphenyldecane}}}{k_{1,2\text{-diphenylethane}}}\right)$
Conditions: 10.5 hours at $70.0 \pm 0.5^\circ\text{C}$; Mmoles $\text{C}_6\text{H}_4\text{Cl}_2$: 2.118						
1	1,10-diphenyldecane	3.551	2.628	0.923	25.99	2.517
	1,2-diphenylethane	2.657	2.358	0.299	11.25	
	BrCCl_3	21.006				
2	1,10-diphenyldecane	3.551	2.206	1.345	37.88	2.636
	1,2-diphenylethane	2.657	2.218	0.439	16.52	
	BrCCl_3	21.006				
3	1,10-diphenyldecane	3.551	1.669	1.882	53.00	2.257
	1,2-diphenylethane	2.657	1.902	0.755	28.42	
	BrCCl_3	21.006				
4	1,10-diphenyldecane	3.551	2.469	1.082	30.47	2.301
	1,2-diphenylethane	2.652	2.269	0.383	14.44	
	BrCCl_3	21.006				
5	1,10-diphenyldecane	3.551	2.173	1.378	38.81	2.381
	1,2-diphenylethane	2.652	2.162	0.490	18.48	
	BrCCl_3	21.006				
6	1,10-diphenyldecane	3.551	1.950	1.601	45.09	2.305
	1,2-diphenylethane	2.652	2.049	0.603	22.74	
	BrCCl_3	21.006				
Average $\left(\frac{k_{1,10\text{-diphenyldecane}}}{k_{1,2\text{-diphenylethane}}}\right) = 2.400 \pm 0.118$						

APPENDIX 5

Kinetic Studies of the Reaction Between 4-Methyl-1-Phenyl-4-(substitutedphenyl)pentanes with Bromotrichloromethane;
Initiated with Light.

Table 44. Relative rate of disappearance of 4-(4-methoxyphenyl)-4-methyl-1-phenylpentane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{(4\text{-methoxyphenyl})}}{k_{\text{diphenylmethane}}}$
Conditions: 70.0 ± 0.5 °C						
1	(4-methoxyphenyl) diphenylmethane BrCCl ₃	1.507 2.634 27.051	1.159 2.142	0.348 0.492	23.07 18.68	1.269
2	(4-methoxyphenyl) diphenylmethane BrCCl ₃	1.507 2.634 27.051	1.196 2.185	0.311 0.449	20.62 17.05	1.235
3	(4-methoxyphenyl) diphenylmethane BrCCl ₃	1.507 2.654 27.051	1.204 2.207	0.303 0.447	20.12 16.98	1.207
4	(4-methoxyphenyl) diphenylmethane BrCCl ₃	1.507 2.634 27.051	0.906 1.785	0.601 0.849	39.87 32.23	1.307
5	(4-methoxyphenyl) diphenylmethane BrCCl ₃	1.507 2.634 27.051	0.886 1.722	0.621 0.912	41.22 34.64	1.249
Average $(k_{4\text{-}(4\text{-methoxyphenyl})\text{-}4\text{-methyl-1-phenylpentane}}/k_{\text{diphenylmethane}}) = 1.253 \pm 0.027$						

Table 45. Relative rate of disappearance of 4-(4-methylphenyl)-4-methyl-1-phenylpentane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{(4\text{-methylphenyl})}}{k_{\text{diphenylmethane}}}$
Conditions: 3 hours 10 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	(4-methylphenyl)	1.663	0.958	0.705	42.39	1.078
	diphenylmethane	2.604	1.561	1.043	40.04	
	BrCCl_3	28.307				
2	(4-methylphenyl)	1.663	0.980	0.683	41.08	1.111
	diphenylmethane	2.604	1.617	0.987	37.89	
	BrCCl_3	28.307				
3	(4-methylphenyl)	1.663	0.798	0.865	52.01	0.979
	diphenylmethane	2.604	1.230	1.374	52.77	
	BrCCl_3	28.307				
4	(4-methylphenyl)	1.663	0.968	0.695	41.80	1.038
	diphenylmethane	2.604	1.546	1.058	40.63	
	BrCCl_3	28.307				
5	(4-methylphenyl)	1.663	1.009	0.654	30.33	1.105
	diphenylmethane	2.604	1.656	0.948	36.39	
	BrCCl_3	28.306				
Average $\left(\frac{k_{(4\text{-methylphenyl})}}{k_{\text{diphenylmethane}}}\right) = 1.062 \pm 0.043$						

Table 46. Relative rate of disappearance of 4-methyl-1, 4-diphenylpentane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{4\text{-methyl...}}}{k_{\text{diphenylmethane}}}\right)$
Conditions: 3 hours 40 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	4-methyl-1, 4- diphenylpentane	1.780	1.026	0.754	36.72	1.112
	diphenylmethane	2.606	1.727	0.879	33.74	
	BrCCl_3	28.384				
2	4-methyl-1, 4- diphenylpentane	1.780	1.084	0.696	39.09	1.129
	diphenylmethane	2.606	1.679	0.927	35.56	
	BrCCl_3	28.384				
3	4-methyl-1, 4- diphenylpentane	1.780	1.061	0.719	40.40	0.990
	diphenylmethane	2.606	1.551	1.055	40.47	
	BrCCl_3	28.384				
4	4-methyl-1, 4- diphenylpentane	1.780	1.015	0.765	43.00	1.047
	diphenylmethane	2.606	1.524	1.082	41.53	
	BrCCl_3	28.384				
5	4-methyl-1, 4- diphenylpentane	1.780	1.095	0.685	38.50	1.028
	diphenylmethane	2.606	1.624	0.982	37.67	
	BrCCl_3	28.384				
6	4-methyl-1, 4- diphenylpentane	1.780	1.253	0.527	29.61	1.107
	diphenylmethane	2.606	1.898	0.708	27.18	
	BrCCl_3	28.384				
7	4-methyl-1, 4- diphenylpentane	1.780	1.157	0.623	34.99	1.031
	diphenylmethane	2.606	1.716	0.890	34.15	
	BrCCl_3	28.384				

(continued)

Table 46. Continued.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{4\text{-methyl-1,4-diphenylpentane}}}{k_{\text{diphenylmethane}}}\right)$
Conditions: 3 hours 20 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	4-methyl-1,4-diphenylpentane	1.981	1.240	0.741	37.42	0.932
	diphenylmethane	2.523	1.527	0.997	39.51	
	BrCCl_3	31.069				
2	4-methyl-1,4-diphenylpentane	1.981	1.276	0.705	35.60	0.982
	diphenylmethane	2.523	1.612	0.911	36.12	
	BrCCl_3	31.069				
3	4-methyl-1,4-diphenylpentane	1.981	1.104	0.877	44.28	1.028
	diphenylmethane	2.523	1.429	1.094	43.38	
	BrCCl_3	31.069				
4	4-methyl-1,4-diphenylpentane	1.981	1.146	0.835	42.15	1.052
	diphenylmethane	2.523	1.419	1.104	43.77	
	BrCCl_3	31.069				
5	4-methyl-1,4-diphenylpentane	1.981	1.368	0.613	30.95	1.057
	diphenylmethane	2.523	1.777	0.746	29.56	
	BrCCl_3	31.069				
Average $\left(\frac{k_{4\text{-methyl-1,4-diphenylpentane}}}{k_{\text{diphenylmethane}}}\right) = 1.041 \pm 0.043$						

Table 47. Relative rate of disappearance of 4-(4-chlorophenyl)-4-methyl-1-phenylpentane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{(4\text{-chlorophenyl})}}{k_{\text{diphenylmethane}}}$
Conditions: 4 hours at $70.0 \pm 0.5^\circ\text{C}$						
1	(4-chlorophenyl)	1.652	0.786	0.866	52.44	0.664
	diphenylmethane	2.786	0.907	1.874	67.37	
	BrCCl_3	29.212				
2	(4-chlorophenyl)	1.652	0.715	0.937	56.74	0.694
	diphenylmethane	2.781	0.835	1.946	69.97	
	BrCCl_3	29.212				
3	(4-chlorophenyl)	1.652	0.866	0.786	47.58	0.641
	diphenylmethane	2.781	1.015	1.766	63.51	
	BrCCl_3	29.212				
4	(4-chlorophenyl)	1.652	0.903	0.749	45.34	0.622
	diphenylmethane	2.781	1.054	1.727	62.11	
	BrCCl_3	29.212				
5	(4-chlorophenyl)	1.652	0.826	0.826	49.98	0.607
	diphenylmethane	2.781	0.888	1.893	68.06	
	BrCCl_3	29.212				
6	(4-chlorophenyl)	1.652	0.764	0.888	53.76	0.678
	diphenylmethane	2.781	0.892	1.889	67.94	
	BrCCl_3	29.212				
7	(4-chlorophenyl)	1.652	0.877	0.775	46.91	0.674
	diphenylmethane	2.781	1.087	1.694	60.93	
	BrCCl_3	29.212				
Average $\left(\frac{k_{4\text{-}(4\text{-chlorophenyl-4-methyl-1-phenylpentane})}}{k_{\text{diphenylmethane}}}\right) = 0.655 \pm 0.027$						

Tabel 48. Relative rate of disappearance of 4-(4-nitrophenyl)-4-methyl-1-phenylpentane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{(4\text{-nitrophenyl})}}{k_{\text{diphenylmethane}}}\right)$
Conditions: 5 hours and 30 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	(4-nitrophenyl) diphenylmethane BrCCl ₃	1.625 2.709 27.585	1.038 1.116	0.587 1.593	36.13 58.81	0.506
2	(4-nitrophenyl) diphenylmethane BrCCl ₃	1.625 2.709 27.585	1.178 1.426	0.447 1.283	27.53 47.37	0.501
3	(4-nitrophenyl) diphenylmethane BrCCl ₃	1.625 2.709 27.585	1.293 1.663	0.332 1.046	20.46 38.62	0.469
4	(4-nitrophenyl) diphenylmethane BrCCl ₃	1.625 2.709 27.585	0.968 0.958	0.657 1.751	40.43 64.62	0.499
5	(4-nitrophenyl) diphenylmethane BrCCl ₃	1.625 2.709 27.585	1.198 1.368	0.427 1.341	26.30 49.49	0.447
6	(4-nitrophenyl) diphenylmethane BrCCl ₃	1.625 2.709 27.585	1.439 2.078	0.186 0.631	11.46 23.31	0.459
Average $\left(\frac{k_{4-(4\text{-nitrophenyl})-4\text{-methyl-1-phenylpentane}}}{k_{\text{diphenylmethane}}}\right) = 0.480 \pm 0.022$						

Table 49. Relative rate of disappearance of 4-(4-bromophenyl)-4-methyl-1-phenylpentane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{(4\text{-bromophenyl})}}{k_{\text{diphenylmethane}}}$
Conditions: 3 hours 30 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	(4-bromophenyl)	1.327	0.745	0.582	43.87	1.308
	diphenylmethane	2.486	1.599	0.887	35.69	
	BrCCl_3	23.215				
2	(4-bromophenyl)	1.327	0.797	0.530	39.92	1.085
	diphenylmethane	2.486	1.554	0.932	37.47	
	BrCCl_3	23.215				
3	(4-bromophenyl)	1.327	0.759	0.568	42.81	1.261
	diphenylmethane	2.486	1.596	0.890	35.81	
	BrCCl_3	23.215				
4	(4-bromophenyl)	1.327	0.706	0.621	46.80	1.087
	diphenylmethane	2.486	1.391	1.095	44.04	
	BrCCl_3	23.215				
5	(4-bromophenyl)	1.327	0.741	0.586	44.18	1.312
	diphenylmethane	2.486	1.594	0.892	35.88	
	BrCCl_3	23.215				
6	(4-bromophenyl)	1.327	0.772	0.555	41.83	1.130
	diphenylmethane	2.486	1.539	0.947	38.09	
	BrCCl_3	23.215				

(continued)

Table 49. Continued.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{(4\text{-bromophenyl})}}{k_{\text{diphenylmethane}}}$
Conditions: 3 hours 30 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	(4-bromophenyl)	1.247	0.647	0.600	48.14	0.941
	diphenylmethane	2.399	1.194	1.205	50.22	
	BrCCl_3	28.884				
2	(4-bromophenyl)	1.247	0.970	0.277	22.18	1.083
	diphenylmethane	2.399	1.903	0.496	20.66	
	BrCCl_3	28.884				
3	(4-bromophenyl)	1.247	0.818	0.429	34.44	0.875
	diphenylmethane	2.399	1.480	0.919	38.29	
	BrCCl_3	28.884				
4	(4-bromophenyl)	1.247	0.651	0.596	47.80	1.076
	diphenylmethane	2.399	1.311	1.088	45.34	
	BrCCl_3	28.884				
5	(4-bromophenyl)	1.247	0.742	0.505	40.50	1.144
	diphenylmethane	2.399	1.524	0.875	36.49	
	BrCCl_3	28.884				
6	(4-bromophenyl)	1.247	0.675	0.572	45.84	1.008
	diphenylmethane	2.399	1.306	1.093	45.58	
	BrCCl_3	28.884				
7	(4-bromophenyl)	1.247	0.723	0.524	42.05	0.916
	diphenylmethane	2.399	1.322	1.077	44.89	
	BrCCl_3	28.884				
Average $\left(\frac{k_{(4\text{-bromophenyl})}}{k_{\text{diphenylmethane}}}\right) = 1.094 \pm 0.105$						

Table 50. Relative rate of disappearance of 4-(2-methoxyphenyl)-4-methyl-1-phenylpentane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{(2\text{-methoxyphenyl})}}{k_{\text{diphenylmethane}}}$
Conditions: 2 hours 55 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	(2-methoxyphenyl)	1.530	0.946	0.584	38.17	1.493
	diphenylmethane	2.664	1.930	0.734	27.54	
	BrCCl_3	27.900				
2	(2-methoxyphenyl)	1.530	0.797	0.733	47.93	1.560
	diphenylmethane	2.664	1.753	0.911	34.19	
	BrCCl_3	27.900				
3	(2-methoxyphenyl)	1.530	0.910	0.620	40.55	1.482
	diphenylmethane	2.664	1.875	0.789	29.60	
	BrCCl_3	27.900				
4	(2-methoxyphenyl)	1.530	0.790	0.740	48.36	1.450
	diphenylmethane	2.664	1.689	0.975	36.60	
	BrCCl_3	27.900				
5	(2-methoxyphenyl)	1.530	0.814	0.716	46.79	1.543
	diphenylmethane	2.664	1.770	0.894	33.56	
	BrCCl_3	27.900				
6	(2-methoxyphenyl)	1.530	0.756	0.774	50.57	1.480
	diphenylmethane	2.664	1.655	1.009	37.86	
	BrCCl_3	27.900				
Average $(k_{4-(2\text{-methoxyphenyl})-4\text{-methyl-1-phenylpentane}} / k_{\text{diphenylmethane}}) = 1.501 \pm 0.033$						

APPENDIX 6

Kinetic Studies of the Reaction Between 4-Phenyl-1-
substitutedbutanes with Bromotrichloromethane;
Initiated with Light

Table 51. Relative rate of disappearance of 1-phenylpentane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1\text{-phenylpentane}}}{k_{\text{diphenylmethane}}}$
Conditions: 3 hours and 55 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	1-phenylpentane	3.623	1.651	1.972	54.43	1.128
	diphenylmethane	3.343	1.665	1.678	50.18	
	BrCCl_3	28.119				
2	1-phenylpentane	3.623	1.318	2.305	63.62	1.074
	diphenylmethane	3.343	1.304	2.039	60.98	
	BrCCl_3	28.119				
3	1-phenylpentane	3.623	1.408	2.215	61.13	1.096
	diphenylmethane	3.343	1.412	1.931	57.77	
	BrCCl_3	28.119				
4	1-phenylpentane	3.623	0.172	3.451	95.26	1.028
	diphenylmethane	3.343	0.172	3.171	94.85	
	BrCCl_3	28.119				
5	1-phenylpentane	3.623	1.212	2.411	66.55	1.093
	diphenylmethane	3.343	1.228	2.115	63.27	
	BrCCl_3	28.119				
6	1-phenylpentane	3.623	1.671	1.952	53.88	1.214
	diphenylmethane	3.343	1.767	1.576	47.14	
	BrCCl_3	28.119				
Average $(k_{1\text{-phenylpentane}}/k_{\text{diphenylmethane}}) = 1.106 \pm 0.043$						

Table 52. Relative rate of disappearance of 1-phenylbutane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{1\text{-phenylbutane}}}{k_{\text{diphenylmethane}}}$
Conditions: 3 hours 20 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	1-phenylbutane	3.439	1.098	2.341	68.08	1.042
	diphenylmethane	2.682	0.897	1.785	66.57	
	BrCCl_3	28.114				
2	1-phenylbutane	3.439	1.221	2.218	64.51	1.019
	diphenylmethane	2.682	0.971	1.711	63.80	
	BrCCl_3	28.114				
3	1-phenylbutane	3.439	1.372	2.067	60.10	1.145
	diphenylmethane	2.682	1.203	1.479	55.16	
	BrCCl_3	28.114				
4	1-phenylbutane	3.439	1.492	1.947	56.62	1.046
	diphenylmethane	2.682	1.207	1.475	55.00	
	BrCCl_3	28.114				
5	1-phenylbutane	3.439	1.015	2.424	70.50	1.094
	diphenylmethane	2.682	0.879	1.803	67.22	
	BrCCl_3	28.114				
Average $\left(\frac{k_{1\text{-phenylbutane}}}{k_{\text{diphenylmethane}}}\right) = 1.069 \pm 0.040$						

Table 53. Relative rate of disappearance of 1-methoxy-4-phenylbutane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-methoxy-}}}{k_{\text{diphenylmethane}}}\right)$
Conditions: 3 hours and 35 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	1-methoxy- diphenylmethane BrCCl_3	2.869	2.086	0.783	27.28	0.833
		2.715	1.852	0.863	31.79	
		30.040				
2	1-methoxy- diphenylmethane BrCCl_3	2.869	2.013	0.856	29.83	0.887
		2.715	1.821	0.894	32.92	
		30.040				
3	1-methoxy- diphenylmethane BrCCl_3	2.869	2.279	0.590	20.57	0.870
		2.715	2.084	0.631	23.25	
		30.040				
4	1-methoxy- diphenylmethane BrCCl_3	2.869	2.021	0.848	29.54	0.897
		2.715	1.838	0.877	32.32	
		30.040				
5	1-methoxy- diphenylmethane BrCCl_3	2.869	2.130	0.739	25.76	0.919
		2.715	1.963	0.752	27.68	
		30.040				
6	1-methoxy- diphenylmethane BrCCl_3	2.869	2.131	0.738	25.72	0.827
		2.715	1.895	0.820	30.20	
		30.040				
Average $\left(\frac{k_{1\text{-methoxy-4-phenylbutane}}}{k_{\text{diphenylmethane}}}\right) = 0.872 \pm 0.029$						

Table 54. Relative rate of disappearance of 1-chloro-4-phenylbutane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1\text{-chloro}}}{k_{\text{diphenylmethane}}}\right)$
Conditions: 70.0 ± 0.5 °C						
1	1-chloro- diphenylmethane CBrCl ₃	2.522	1.959	0.563	22.32	0.573
		2.478	1.594	0.884	35.66	
		28.387				
2	1-chloro- diphenylmethane CBrCl ₃	2.522	1.704	0.818	32.45	0.617
		2.478	1.312	1.166	47.06	
		28.387				
3	1-chloro- diphenylmethane CBrCl ₃	2.522	1.603	0.919	36.44	0.529
		2.478	1.051	1.427	57.57	
		28.387				
4	1-chloro- diphenylmethane CBrCl ₃	2.522	1.551	0.971	38.50	0.537
		2.478	1.003	1.475	59.52	
		28.387				
5	1-chloro- diphenylmethane CBrCl ₃	2.522	1.745	0.777	30.82	0.576
		2.478	1.306	1.172	47.28	
		28.387				
6	1-chloro- diphenylmethane CBrCl ₃	2.522	1.805	0.717	28.44	0.603
		2.478	1.423	1.055	42.57	
		28.387				
Average $\left(\frac{k_{1\text{-chloro-4-phenylbutane}}}{k_{\text{diphenylmethane}}}\right) = 0.572 \pm 0.026$						

Table 55. Relative rate of disappearance of ethyl 5-phenylpentanoate vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{\text{ethyl 5-phenyl-}}}{k_{\text{diphenylmethane}}} \right)$
Conditions: 3 hours and 45 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	ethyl 5-phenylpentanoate	2.210	1.533	0.677	30.65	0.540
	diphenylmethane	2.646	1.343	1.303	49.25	
	BrCCl_3	27.742				
2	ethyl 5-phenylpentanoate	2.210	1.504	0.706	31.96	0.570
	diphenylmethane	2.646	1.347	1.299	49.10	
	BrCCl_3	27.742				
3	ethyl 5-phenylpentanoate	2.210	1.547	0.663	29.98	0.537
	diphenylmethane	2.646	1.363	1.283	48.48	
	BrCCl_3	27.742				
Conditions: 4 hours and 15 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	ethyl 5-phenylpentanoate	2.091	1.399	0.692	33.10	0.577
	diphenylmethane	2.670	1.330	1.340	50.19	
	BrCCl_3	28.208				
2	ethyl 5-phenylpentanoate	2.091	1.575	0.516	24.70	0.533
	diphenylmethane	2.670	1.568	1.102	41.26	
	BrCCl_3	28.208				
3	ethyl 5-phenylpentanoate	2.091	1.430	0.661	31.59	0.533
	diphenylmethane	2.670	1.311	1.359	50.91	
	BrCCl_3	28.208				
4	ethyl 5-phenylpentanoate	2.091	1.351	0.740	35.39	0.563
	diphenylmethane	2.670	1.228	1.442	53.99	
	BrCCl_3	28.208				
Average $\left(\frac{k_{\text{ethyl 5-phenylpentanoate}}}{k_{\text{diphenylmethane}}} \right) = 0.550 \pm 0.017$						

Table 56. Relative rate of disappearance of 5-phenylpentanonitrile vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\frac{k_{5\text{-phenylpentano-}}}{k_{\text{diphenylmethane}}}$
Conditions: 3 hours at $70.0 \pm 0.5^\circ\text{C}$						
1	5-phenyl- diphenylmethane BrCCl_3	2.812	2.221	0.591	21.00	0.416
		2.681	1.522	1.159	43.24	
		29.330				
2	5-phenyl- diphenylmethane BrCCl_3	2.812	2.158	0.654	23.24	0.359
		2.681	1.283	1.398	52.16	
		29.330				
3	5-phenyl- diphenylmethane BrCCl_3	2.812	2.282	0.530	18.86	0.384
		2.681	1.555	1.126	42.01	
		29.330				
4	5-phenyl- diphenylmethane BrCCl_3	2.812	2.238	0.574	20.40	0.318
		2.681	1.308	1.373	51.21	
		29.330				
5	5-phenyl- diphenylmethane BrCCl_3	2.812	2.156	0.656	23.33	0.425
		2.681	1.434	1.247	46.50	
		29.330				
6	5-phenyl- diphenylmethane BrCCl_3	2.812	2.059	0.753	26.77	0.322
		2.681	1.020	1.661	61.97	
		29.330				
Average $\left(\frac{k_{5\text{-phenylpentanonitrile}}}{k_{\text{diphenylmethane}}} \right) = 0.371 \pm 0.038$						

Table 57. Relative rate of disappearance of 1,4-diphenylbutane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,4\text{-diphenylbutane}}}{k_{\text{diphenylmethane}}}\right)$
Conditions: 3 hours 15 minutes at $70.0 \pm 0.5^\circ\text{C}$						
1	1,4-diphenylbutane	2.085	1.618	0.467	22.39	0.714
	diphenylmethane	2.849	1.998	0.851	29.88	
	BrCCl_3	28.323				
2	1,4-diphenylbutane	2.085	1.473	0.612	29.36	0.758
	diphenylmethane	2.849	1.802	1.047	36.76	
	BrCCl_3	28.323				
3	1,4-diphenylbutane	2.085	1.618	0.467	22.38	0.831
	diphenylmethane	2.849	2.101	0.748	26.26	
	BrCCl_3	28.323				
4	1,4-diphenylbutane	2.085	1.501	0.584	28.01	0.753
	diphenylmethane	2.849	1.842	1.007	35.36	
	BrCCl_3	28.323				
5	1,4-diphenylbutane	2.085	1.451	0.634	30.42	0.765
	diphenylmethane	2.849	1.773	1.076	37.76	
	BrCCl_3	28.323				
6	1,4-diphenylbutane	2.085	1.588	0.497	23.84	0.740
	diphenylmethane	2.849	1.972	0.877	30.79	
	BrCCl_3	28.323				
Average $\left(\frac{k_{1,4\text{-diphenylbutane}}}{k_{\text{diphenylmethane}}}\right) = 0.760 \pm 0.025$						

Table 58. Relative rate of disappearance of 1,6-diphenylhexane vs diphenylmethane; light initiation.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% xr	$\left(\frac{k_{1,6\text{-diphenylhexane}}}{k_{\text{diphenylmethane}}}\right)$
Conditions: 4 hours at $70.0 \pm 0.5^\circ\text{C}$						
1	1,6-diphenylhexane	1.912	1.184	0.728	38.09	0.914
	diphenylmethane	2.653	1.570	1.083	40.82	
	BrCCl_3	27.982				
2	1,6-diphenylhexane	1.912	1.204	0.708	37.02	0.977
	diphenylmethane	2.653	1.653	1.000	37.70	
	BrCCl_3	27.982				
3	1,6-diphenylhexane	1.912	1.462	0.450	23.54	0.857
	diphenylmethane	2.653	1.939	0.714	26.90	
	BrCCl_3	27.982				
4	1,6-diphenylhexane	1.912	1.289	0.623	32.58	0.933
	diphenylmethane	2.653	1.739	0.914	34.46	
	BrCCl_3	27.982				
5	1,6-diphenylhexane	1.912	1.126	0.786	41.13	0.873
	diphenylmethane	2.653	1.446	1.207	45.49	
	BrCCl_3	27.982				
6	1,6-diphenylhexane	1.912	1.120	0.792	41.40	0.937
	diphenylmethane	2.653	1.500	1.153	43.47	
	BrCCl_3	27.982				
Average $\left(\frac{k_{1,6\text{-diphenylhexane}}}{k_{\text{diphenylmethane}}}\right) = 0.915 \pm 0.034$						