1963

Directive effects in abstraction reactions of the phenyl radical

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Recommended Citation

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BRIDGER, Robert Frederick, 1934–
DIRECTIVE EFFECTS IN ABSTRACTION REACTIONS OF THE PHENYL RADICAL.

Iowa State University of Science and Technology
Ph.D., 1963
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

DIRECTIVE EFFECTS IN ABSTRACTION REACTIONS OF THE PHENYL RADICAL

by

Robert Frederick Bridger

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1963

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INTRODUCTION

The results summarized in this thesis represent an effort to obtain rudimentary information about abstraction reactions of the phenyl radical. Because of the experimental difficulties involved in measuring absolute rates of free radical reactions in solution, the method of competitive reactions is generally used as an approach to such problems (1). In the competetive method two compounds are allowed to compete for some reactive intermediate, whose concentration may be quite small in comparison with the concentration of the competing substrates. The necessary experimental data are similar to those required in a kinetic study, except that the time variable has been eliminated. Experimentally all that is required is a method of measuring either the disappearance of the substrates or the appearance of products. In the present study this was accomplished by gas phase chromatography and ultraviolet absorption.

The data obtained from such a study have the form of relative rates or relative reactivities and reflect the selectivity of the reactive intermediate. By determining the relative rates of reaction of appropriate model compounds it is possible to arrive at conclusions regarding the influence of molecular structure on the reactivities of individual bonds. Comparison of the selectivity of the reactive intermediate with similar data for other radicals permits at least qualitative conclusions to be drawn concerning the reactivities of the radicals and the nature of the transition states involved in their reactions, particularly those involving atom transfer or abstraction.

Abstraction reactions, also called methothetical or transfer reactions, may be represented by the equation

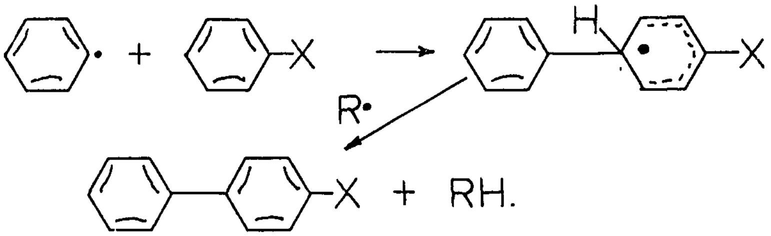
$$R_1^{\bullet} + R_2X \longrightarrow R_1X + R_2^{\bullet} \quad . \qquad (1)$$

A discussion of directive effects in such processes must include those factors influencing the site and velocity of radical attack in both intramolecular and intermolecular competition reactions.

In the present study phenyl radicals were generated by the thermal decomposition of phenylazotriphenylmethane. The relative reactivities of III compounds toward the phenyl radical were investigated by the method of competitive reactions using carbon tetrachloride as the reference solvent. All reactions were conducted at 60 °C. The compounds studied were of various types: alkanes, alkenes, alkynes, aromatic hydrocarbons, heteroaromatic compounds, compounds containing functional groups, and compounds containing hydrogen bonded to heteroatoms.

LITERATURE REVIEW

Previous studies of reactions of the phenyl radical have concentrated almost exclusively on the addition of various aryl radicals to aromatic systems. The voluminous literature of homolytic arylation has been adequately reviewed (2 - 8), and brief discussion will be given only to those results which have a direct bearing on the problem at hand. The mechanism of aromatic phenylation may be represented by



(2)

While additional intermediates have been proposed (2) and side reactions discussed (3, 9), Equation 2 represents the essential steps of the reaction. The phenyl group usually enters predominantly at the *ortho* and *para* positions of substituted benzenes regardless of the nature of the substituent X. Biphenyl resulting from the coupling of two phenyl radicals is seldom isolated as a reaction product (10).

Two frequently used sources of phenyl radicals are phenylazotriphenylmethane (PAT) and benzoyl peroxide. When phenyl radicals are generated thermally from benzoyl peroxide, the role of R· in Equation 1 is filled by benzoyloxy and phenyl radicals, giving rise to benzoic acid and benzene in addition to biphenyls and more complicated products (3, 11). The use of PAT as a phenyl generator results in the formation of biphenyl, tetraphenylmethane, and triphenylmethane (12), the last arising by the acceptance of hydrogen from the intermediate complex by the trityl radical. Recent results of Eliel and coworkers (9) suggest that, in the case of PAT, removal of the hydrogen atom from the phenylcyclohexadienyl radical is accomplished by the triphenylmethyl radical exclusively.

Experiments (13, 14) with substituted aryl radicals indicate that the phenyl radical is a neutral species (i.e., no strong polarization) and its electronic demands in the transition state(s) should be about the same as those of an alkyl radical (3). Recently Waters and coworkers (15) determined isomer distributions resulting from homolytic methylation of five substituted benzenes. While the pattern was similar to that obtained by previous workers for homolytic phenylation, the differences led Waters to suggest an order of electrophilicity: $CH_3 < C_6H_5 < C_6H_4Cl < C_6H_4NO_2$.

The occurrence of side chain attack (3, 13, 11) by phenyl radicals in reactions with aralkyl hydrocarbons has been frequently reported, as has the attack of phenyl radicals on aliphatic solvents. A quantitative investigation of these latter reactions has been reported recently (16). At the present time no systematic investigation of abstraction reactions of the phenyl radical has appeared in the literature.

RESULTS

The thermal decomposition of phenylazotriphenylmethane (PAT) in a mixture of two solvents may be represented by the following equations:

$$\text{Ph-N=N-CPh}_3 \longrightarrow \text{Ph}^{\cdot} + \text{N}_2 + \text{Ph}_3\text{C}^{\cdot} \qquad (3)$$

$$\text{Ph}\cdot + \text{CCl}_4 \xrightarrow{4k_{(\text{Cl})}} \text{PhCl} + \text{Cl}_3\text{C}\cdot \qquad (4)$$

$$\text{Ph}\cdot + \text{RH} \xrightarrow{\Sigma n_i k_{i(\text{H})}} \text{PhH} + \text{R}\cdot \qquad (5)$$

$$\text{Ph}_3\text{C}\cdot + \text{Cl}_3\text{C}\cdot + \text{R}\cdot \longrightarrow \text{Non-radical products} \quad , \qquad (6)$$

where Ph = C_6H_5,

RH = an organic compound capable of transferring hydrogen atoms to the phenyl radical,

$k_{(Cl)}$ = rate constant for abstraction reaction at a single carbon-chlorine bond of carbon tetrachloride,

$k_{i(H)}$ = rate constant for abstraction at a carbon-hydrogen bond of order (type) i,

and n_i = number of carbon-hydrogen bonds of order (type) i .

The kinetic expressions may be reduced to

$$\frac{\Sigma n_i k_{i(\text{H})}}{4k_{(\text{Cl})}} = \frac{(\text{PhH})(\text{CCl}_4)}{(\text{PhCl})(\text{RH})} \quad . \qquad (7)$$

Three assumptions are involved in the derivation of Equation 7: (a) Reactions 4 and 5 are each of the same molecularity in phenyl radical concentration and unimolecular in the concentration of the substrate. (b) Reactions 4 and 5 are the only source of chlorobenzene and benzene, respectively. (c) The ratio of the concentrations of carbon tetrachloride and the hydrogen-containing substrate remains constant.

An experimental test of the first and second assumptions is afforded by varying the concentrations of carbon tetrachloride and the hydrocarbon (or hydrogen-containing substrate). Examination of the data in Table 1 shows that varying the ratio $(CCl_4)/(RH)$ has no effect upon the ratio of rate constants within experimental error. Other examples of variation in the molar ratio of substrates appear in Table 2.

A further test of assumptions (a) and (b) can be made considering the effect of initial PAT concentration on the observed ratio of k_H/k_{Cl}. Increasing the initial PAT concentration will increase the average pheny radical concentration (assumption a). On the other hand, if either benzene or chlorobenzene is a product of reactions that are bimolecular or higher kinetic order in radicals (e.g., Reaction 8),

$$Ph\cdot + \cdot CCl_3 \longrightarrow PhCl + CCl_2 \qquad (8)$$

Table 1. Decompositions of PAT in carbon tetrachloride-hydrocarbon solutions at 60 °C

Hydrocarbon	Conc. PAT, mole/liter	$\frac{(CCl_4)}{(RH)}$	$\frac{k_H}{k_{Cl}}$
Toluene	0.096	0.552	0.36
Toluene	0.096	0.735	0.36
Toluene	0.096	0.965	0.36
Toluene	0.096	1.26	0.35
Cyclohexane	0.096	0.748	0.36
Cyclohexane	0.096	0.985	0.36
Cyclohexane	0.096	1.680	0.36
Cyclohexane	0.051	0.985	0.36
Cyclohexane	0.180	0.985	0.34

or product of a reaction of a phenyl radical with an initially formed highly reactive product (e.g., Reaction 9),

$$Ph\cdot + Ph_3C\text{-}CCl_3 \longrightarrow PhCl + Ph_3C\text{-}Cl_2\cdot \qquad (9)$$

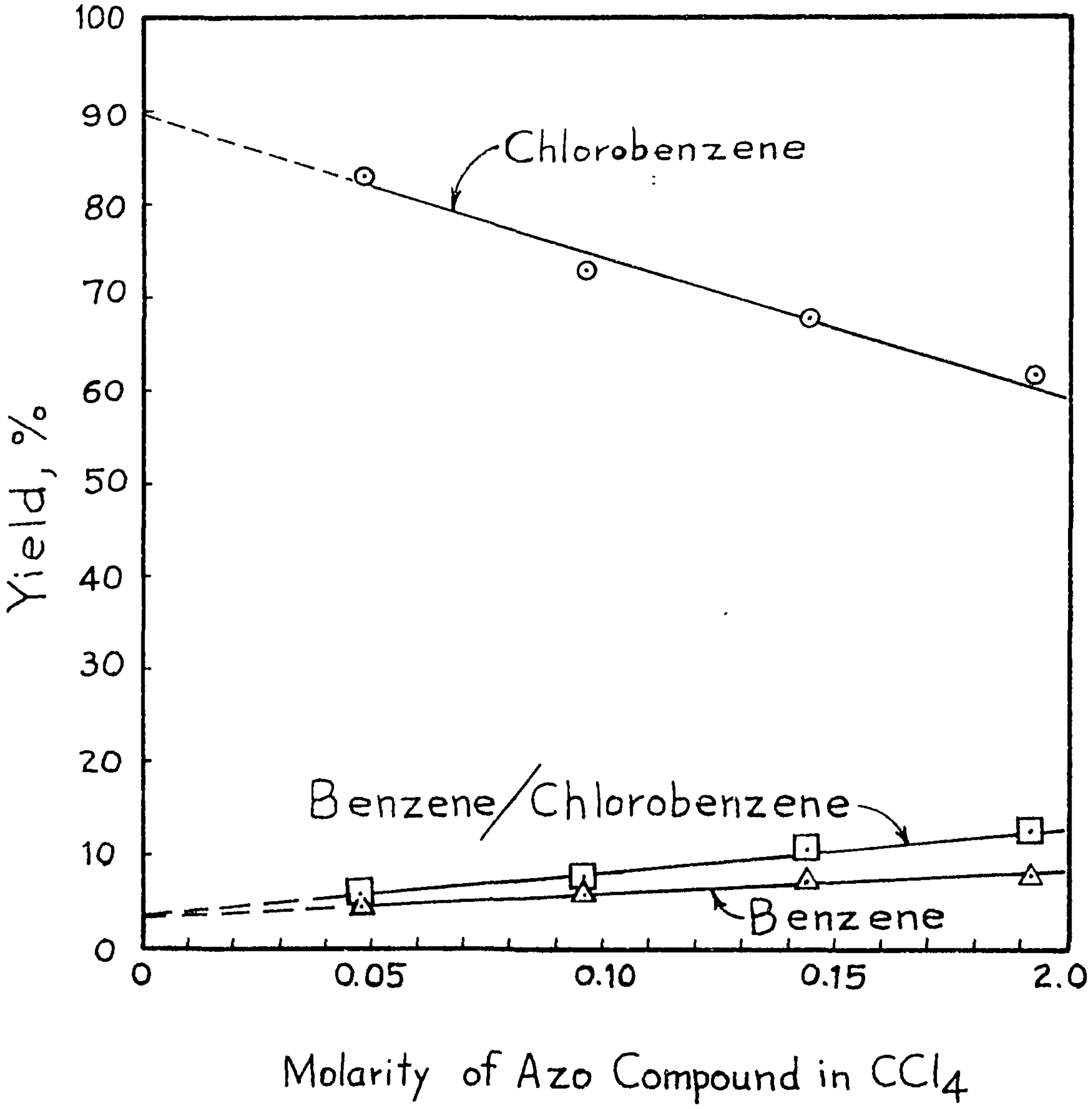
then the observed ratio k_H/k_{Cl} will vary in a systematic manner with a change in the initial concentration of PAT. That assumptions (a) and (b) are indeed valid is substantiated by the data of Table 1 wherein the calculated value of k_H/k_{Cl} is shown to be independent of initial PAT concentration at a constant ratio of $(CCl_4)/(RH)$.

The third approximation may be controlled by proper choice of experimental conditions. Decomposition of a 0.1 M solution of PAT in a solvent composed of equimolar amounts of carbon tetrachloride and a hydrocarbon of approximately equal reactivity decreases the concentration of each solvent by no more than one per cent and will affect the ratio $(CCl_4)/(RH)$ even less. The value of one per cent is based upon the presumption that only one mole of carbon tetrachloride or hydrocarbon is consumed for each mole of chlorobenzene or benzene found after complete decomposition of the PAT. It will be shown later that the maximum yield of chlorobenzene and benzene observed under the experimentally chosen reaction conditions is in the range of 60 - 80%.

Equations 3 through 6 do not predict the formation of even traces of benzene during the decomposition of PAT in pure carbon tetrachloride. However, as shown in Figure 1, benzene is always a reaction product although it is formed in low yield.

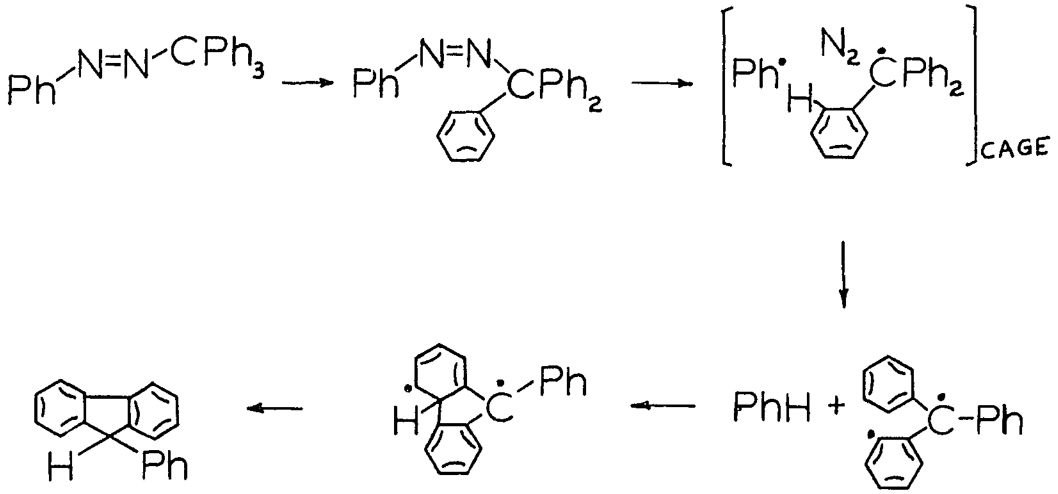
The formation of benzene during decomposition of PAT in carbon tetrachloride cannot be explained at present. Since the carbon tetrachloride was of excellent purity the formation of benzene must be attributed to hydrogen donation by PAT or some impurity therein, or result as a primary decomposition product, possibly as a result of a cage reaction.

Figure 1. Decomposition of phenylazotriphenylmethane in carbon tetrachloride at 60 °C


Yield, %
100
90
80
70
60
50
40
30
20
10
0
0
0.05
0.10
0.15
2.0
Chlorobenzene
Benzene/Chlorobenzene
Benzene
Molarity of Azo Compound in CCl4

The most likely possibility is donation of hydrogen by N-phenyl-N'-tritylhydrazine. Indeed, decomposition in carbon tetrachloride of impure PAT containing ca. 55 per cent of the hydrazine resulted in equal yields of benzene and chlorobenzene. However, treatment of the azo compound with a variety of oxidizing agents failed to reduce the yield of benzene significantly below the correction value of 0.054 mole/mole PAT when initial PAT concentration is 0.1 M. It is believed that the PAT used in this study was free of N-phenyl-N'-tritylhydrazine. (See Experimental section for details.)

As shown in Figure 1, the extrapolation of the straight line for benzene yield to zero PAT concentration does not pass through the origin. Such behavior strongly suggests the occurrence of a cage reaction yielding benzene. One possibility, for which no evidence exists, is shown below.



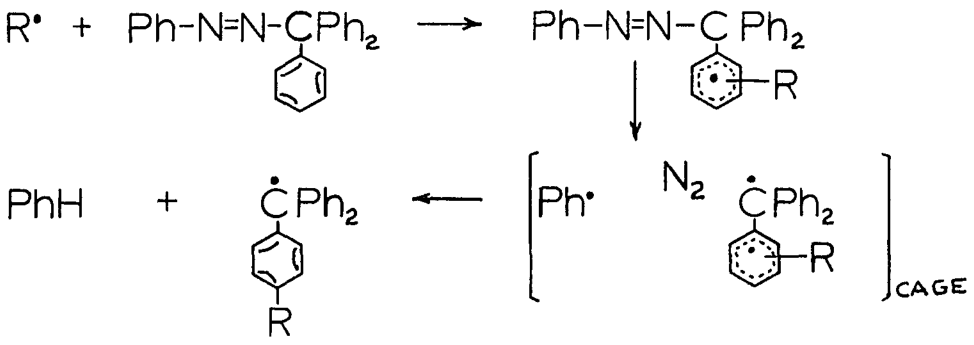
(10)

The migration of hydrogen to the *alpha* carbon required in Equation 10 may involve more steps than shown above; an analogy may be found in the formation of Chichibabin's hydrocarbon from the triphenylmethyl radical (17).

Although the yield of benzene does not approach zero, the yield of benzene does nevertheless vary slightly with initial PAT concentration. This suggests a second route to benzene involving a reaction of some radical with PAT itself or one of its decomposition products. Among possible reactions the following may be listed.

$$\mathrm{Ph}^{\bullet} + \mathrm{PAT} \longrightarrow \mathrm{PhH} + \mathrm{PAT(-H)}^{\bullet} \quad , \tag{11}$$

and



(12)

When R = Ph_3C, Reaction Sequence 12 assumes a resemblance to the Wieland reaction (3, 17).

Walling (18) has reported the formation of 0.06 moles benzene per mole of peroxide during the decomposition of benzoyl peroxide in carbon tetrachloride at 70 °C. His material balance accounted for 95 per cent of the peroxide decomposed, the remainder representing "some unidentified dehydrogenated product equivalent to the benzene formed". A more satisfying explanation is not forthcoming.

In the study of hydrogen abstraction reactions by phenyl radicals, the yield of benzene obtained experimentally from the decomposition of 0.1 M PAT has been corrected by subtracting 0.054 mole of benzene per mole of PAT, the total amount of benzene formed in the decomposition of PAT in pure carbon tetrachloride solution.

The assumption that a correction of -0.054 is independent of solvent is well justified by the results of decomposition of PAT in various aromatic compounds (Reactions 65 - 67, Table 2; and decomposition in chlorobenzene neat, Table 3). Moreover, these results prove that benzene does not arise from any simple homolytic aromatic substitution process, since the yield of benzene does not significantly increase when the solvent is changed from carbon tetrachloride to pure chlorobenzene or to mixtures of carbon tetrachloride with diphenyl ether, biphenyl, or triphenylamine. The same type of correction was used by DeTar and Wells (19) in a similar study to correct for the disproportionation of the 1-hexyl radical in carbon tetrachloride solution. While casting the benzene correction in another form or omitting it altogether would slightly alter the quantitative results, the conclusions based on the data reported herein would not be significantly changed.

The fates of the radicals trityl, trichloromethyl, and R• (Equation 6) have been elucidated by Hey and Peters (16), who isolated and characterized most of the decomposition products of PAT and benzoyl peroxide in a variety of aliphatic solvents. In the presence of relatively high concentrations of trityl radicals the following reactions predominate:

$$Ph_3C\cdot + R\cdot \longrightarrow Ph_3C{-}R \qquad (13)$$

$$Ph_3C\cdot + Cl_3C\cdot \longrightarrow Ph_3C{-}CCl_3 \quad . \qquad (14)$$

The products of Reactions 13 and 14 were isolated by Hey and Peters and, with the exceptions of triphenylmethane and tetraphenylmethane, were the only non-volatile products isolated from decompositions of phenylazotriphenylmethane. No hexachloroethane was detected in reactions of PAT. Hey and Peters did not detect benzene (by nitration procedure) from the decomposition of PAT in carbon tetrachloride. However, they attributed the formation of triphenylmethane to the presence of benzene and ethanol (recrystallization solvents) in the azo compound.

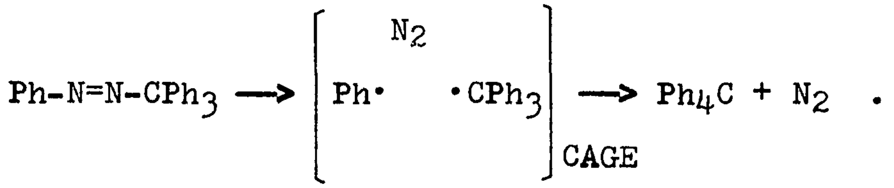
Russell (20) has determined the chain length to be 16 for the peroxide induced reaction between carbon tetrachloride and cyclohexane:

$$CCl_4 + R\cdot \longrightarrow RCl + Cl_3C\cdot \qquad (15)$$

$$Cl_3C\cdot + RH \longrightarrow CHCl_3 + R\cdot \qquad (16)$$

In the present study chloroform was detected only in reactions of three or four compounds possessing extremely reactive carbon-hydrogen bonds, and yields were less than unity. The yields of alkyl chlorides arising from competitive reactions of alkanes in carbon tetrachloride never exceeded unity and in general were less than 0.25 mole/mole PAT. This is attributed to the absence of chain reactions due to the high concentrations of trityl radicals (Equations 13 and 14). Thus the difficulties which have plaqued previous workers (19, 21) using peroxides were obviated by the choice of radical generator.

Although it was not a major object of this study to determine the maximum yield of free phenyl radicals obtainable from PAT, the results indicate a maximum yield of 80 - 90%. Thus, from Figure 1, a linear extrapolation of the chlorobenzene yield to zero PAT concentration gives a 90% yield of chlorobenzene. In isopropyl alcohol containing copper (II) chloride (moles $CuCl_2$/mole PAT = 3) 84% yield of chlorobenzene and 10% yield of benzene were observed. If the 5.4% correction for spurious benzene is applied, this experiment indicates an 88.6% yield of phenyl radicals. It is well known (22) that copper (II) chloride is extremely reactive and therefore an efficient transfer agent for free radicals. The remaining 10% of the phenyl radicals are consumed in the reaction giving rise to benzene which occurs even in pure carbon tetrachloride solution and in still another cage reaction (16) leading to tetraphenylmethane.



$$\mathrm{Ph{-}N{=}N{-}CPh_3} \longrightarrow \left[\begin{array}{ccc} & \mathrm{N_2} & \\ \mathrm{Ph\cdot} & & \mathrm{\cdot CPh_3} \\ & & \end{array}\right]_{\mathrm{CAGE}} \longrightarrow \mathrm{Ph_4C} + \mathrm{N_2} \quad . \qquad (17)$$

The reactivities of a number of carbon-hydrogen bonds toward phenyl radicals have been determined by using a standard technique which is described in detail in the experimental section. This technique involved the complete decomposition of a 0.1 M solution of PAT in a mixture of carbon tetrachloride (reference) and the hydrogen-containing substrate at 60 °C, followed by determination of benzene and chlorobenzene by gas phase chromatography or ultraviolet absorption.

Three definitions will be used throughout this thesis:

1. Total reactivity, or reactivity per molecule, of compound RH is the reactivity toward phenyl radical relative to that of carbon tetrachloride, the reference solvent. It is defined by

$$\begin{array}{l}\text{Total}\\ \text{reactivity}\end{array} = \frac{\Sigma n_i k_{i(H)}}{4k_{(Cl)}} = \frac{(\mathrm{CCl_4})(\mathrm{PhH}-0.054)}{(\mathrm{RH})(\mathrm{PhCl})} \qquad (18)$$

The correction of -0.054 applied to benzene arises from the production of benzene during decomposition of 0.1 M PAT in pure carbon tetrachloride (see above). Because the volume of the reaction mixture remains constant, mole ratios are used for carbon tetrachloride and the hydrogen-containing substrate. Yields of benzene and chlorobenzene are expressed in moles/mole PAT.

2. Reactivity per bond is that value obtained for reactivity after statistical corrections have been made for the number of bonds in RH and CCl_4. For a carbon-hydrogen bond of type i it is equal to $k_{i(H)}/k_{(Cl)}$.
3. Enhancement of reactivity is defined as reactivity per bond divided by the reactivity of the analogous paraffinic carbon-hydrogen bond.

The precision of the data varies somewhat, depending upon the reactivity of the compound under investigation. Using the range of duplicate or multiple determinations as a measure of precision, the following relative errors in the total reactivities apply to different types of compounds: alkanes, ± 3%; aromatic hydrocarbons, ± 3 to 15%; olefins, ± 4%; compounds containing functional groups, ± 5%. Errors become magnified in the determination of reactivities per bond, which must be calculated from simultaneous equations involving total reactivities. Extremely unreactive compounds will yield poorer precision than listed above. The value for diphenylphosphine is a rather questionable estimate of order of magnitude because of side reactions (see Experimental).

All data are summarized in tabular form on the following pages. The order of appearance in Table 2 is according to types of compounds and reactivities. Although arbitrary, this numbered order is convenient for purposes of discussion and will be followed throughout this thesis.

Table 2. Reactivities of selected compounds toward the phenyl radical at 60 °C

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
1a	Dimethylpropane	0.856	0.129	0.466	0.60	0.138
1b	"	0.880	0.124	0.466	0.59	0.132
2a	Tetramethylbutane	1.516	0.144	0.592	0.73	0.230
2b	"	0.895	0.173	0.516	0.68	0.206
2c	"	0.858	0.146	0.458	0.60	0.170
3a	Pentane	1.05	0.297	0.422	0.72	0.605
3b	"	1.05	0.283	0.417	0.70	0.578
4a	Hexane	0.904	0.367	0.355	0.73	0.797
4b	"	0.904	0.355	0.351	0.71	0.777
5a	Heptane	1.012	0.386	0.351	0.74	0.959
5b	"	1.012	0.377	0.345	0.72	0.947
6a	Octane	1.125	0.427	0.361	0.79	1.16
6b	"	1.125	0.405	0.358	0.77	1.10
7a	Hexadecane	2.74	0.391	0.365	0.76	2.53
7b	"	2.74	0.389	0.369	0.75	2.49

---

[a] Mole/mole PAT.

[b] $\frac{\Sigma n_i k_i(H)}{4k(Cl)} = \frac{(CCl_4)(PhH-0.054)}{(RH)(PhCl)}$.

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
8a	2,2-Dimethylbutane	0.917	0.199	0.453	0.65	0.294
8b	"	0.917	0.198	0.443	0.64	0.297
9a	3-Methylpentane	0.898	0.357	0.307	0.67	0.888
9b	"	0.898	0.352	0.300	0.65	0.892
10a	2-Methylpentane	0.920	0.377	0.338	0.72	0.879
10b	"	0.920	0.383	0.359	0.74	0.843
11a	3-Methylhexane	1.01	0.404	0.326	0.73	1.08
11b	"	1.01	0.406	0.336	0.75	1.06
12a	2,3-Dimethylbutane	0.900	0.445	0.306	0.75	1.15
12b	"	0.900	0.429	0.283	0.71	1.19
13a	2,4-Dimethylpentane	1.03	0.303	0.384	0.69	0.668
13b	"	1.03	0.301	0.390	0.69	0.652
14a	2,5-Dimethylhexane	1.027	0.409	0.289	0.70	1.26
14b	"	1.027	0.420	0.296	0.72	1.27
15a	2,2,3-Trimethylbutane	1.002	0.291	0.335	0.63	0.708
15b	"	1.002	0.323	0.379	0.70	0.711
16a	2,2,4-Trimethylpentane	1.142	0.194	0.436	0.63	0.366
16b	"	1.142	0.193	0.484	0.67	0.328
17a	2,2,5-Trimethylhexane	1.252	0.306	0.376	0.68	0.840
17b	"	1.252	0.304	0.404	0.71	0.774

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
18a	2,3,4-Trimethylpentane	1.10	0.369	0.350	0.72	0.990
18b	"	1.10	0.372	0.378	0.75	0.925
19a	Cyclopentane	0.651	0.496	0.280	0.78	1.03
19b	"	0.651	0.503	0.279	0.78	1.05
20a	Cyclohexane	0.748	0.471	0.290	0.76	1.076
20b	"	0.985	0.427	0.338	0.77	1.086
20c	"	1.680	0.335	0.437	0.78	1.083
21a	Cycloheptane	1.005	0.588	0.237	0.83	2.27
21b	"	1.005	0.583	0.234	0.81	2.27
22a	Cyclooctane	0.926	0.585	0.171	0.76	2.87
22b	"	0.926	0.611	0.181	0.79	2.85
23a	Methylcyclopentane	1.020	0.446	0.263	0.71	1.52
23b	"	1.020	0.456	0.268	0.73	1.53
24a	Methylcyclohexane	1.160	0.465	0.309	0.77	1.54
24b	"	1.160	0.458	0.305	0.77	1.54
25a	*cis*-2-Butene	0.813	0.271	0.202	0.47	0.873
25b	"	0.945	0.265	0.238	0.50	0.838
26a	*trans*-2-Butene	0.909	0.210	0.231	0.44	0.614
26b	"	0.912	0.210	0.228	0.44	0.624

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
27a	2-Methyl-2-butene	1.097	0.287	0.211	0.50	1.21
27b	"	1.097	0.287	0.208	0.50	1.23
28a	2,3-Dimethyl-2-butene	1.85	0.422	0.293	0.72	2.32
28b	"	1.85	0.406	0.297	0.70	2.19
29a	1-Butene	0.888	0.166	0.162	0.33	0.614
29b	"	0.885	0.170	0.157	0.33	0.654
30a	1-Pentene	1.150	0.162	0.177	0.34	0.702
30b	"	1.150	0.166	0.179	0.35	0.720
31a	2-Pentene	1.122	0.342	0.257	0.60	1.26
31b	"	1.122	0.357	0.261	0.62	1.30
32a	1-Octene	1.90	0.207	0.221	0.43	1.31
32b	"	1.90	0.207	0.221	0.43	1.31
33a	2-Octene	1.89	0.269	0.256	0.53	1.59
33b	"	1.89	0.271	0.259	0.53	1.58
34a	2-Methyl-1-butene	1.135	0.142	0.112	0.25	0.892
34b	"	1.135	0.140	0.113	0.25	0.865
35a	3-Methyl-1-butene	0.895	0.273	0.134	0.41	1.46
35b	"	0.895	0.258	0.131	0.39	1.39
36a	4-Methyl-2-pentene	1.967	0.324	0.378	0.70	1.40
36b	"	1.967	0.342	0.375	0.72	1.51

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
37a	Propene	0.888	0.065	0.211	0.28	--
37b	"	0.896	0.069	0.220	0.29	--
38a	2,3,3-Trimethyl-1-butene	0.965	0.049	0.102	0.15	--
38b	"	0.965	0.048	0.103	0.15	--
39a	3,3-Dimethyl-1-butene	1.08	0.046	0.209	0.26	--
39b	"	1.08	0.045	0.217	0.26	--
40a	1,3-Pentadiene	1.04	0.026	0.027	0.05	--
40b	"	1.04	0.028	0.033	0.06	--
41a	2-Phenylpropene	1.078	0.013	0.053	0.07	--
41b	"	1.078	0.017	0.053	0.07	--
42a	1-Phenylpropene	1.353	0.065	0.137	0.20	--
42b	"	1.353	0.063	0.122	0.18	--
43a	Cyclopentene	3.68	0.369	0.323	0.69	3.59
43b	"	3.68	0.354	0.312	0.67	3.54
43c	"	3.67	0.355	0.314	0.67	3.52
43d	"	3.67	0.359	0.312	0.67	3.59
44a	Cyclohexene	4.20	0.415	0.348	0.76	4.36
44b	"	4.20	0.410	0.344	0.75	4.35
44c	"	4.07	0.405	0.332	0.74	4.30
44d	"	4.07	0.415	0.339	0.75	4.33

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
45a	3-Phenylpropene	1.37	0.271	0.167	0.44	1.78
45b	"	1.37	0.269	0.163	0.43	1.81
46a	2,5-Dimethyl-2,4-hexadiene	2.50	0.298	0.218	0.52	2.80
46b	"	2.50	0.296	0.197	0.49	3.07
47	Propyne	0.660	0.147	0.227	0.37	0.27
48a	1-Butyne	0.888	0.296	0.210	0.51	1.02
48b	"	0.830	0.298	0.213	0.51	0.95
49a	2-Butyne	0.928	0.364	0.337	0.70	0.854
49b	"	0.873	0.388	0.329	0.72	0.886
50a	*t*-Butylbenzene	1.428	0.102	0.604	0.71	0.114
50b	"	0.814	0.110	0.488	0.60	0.093
51a	Toluene	0.552	0.216	0.328	0.54	0.273
51b	"	0.735	0.198	0.395	0.59	0.268
51c	"	0.965	0.184	0.470	0.65	0.267
51d	"	1.26	0.160	0.512	0.67	0.261
52a	p-Chlorotoluene	1.073	0.178	0.481	0.66	0.276
52b	"	1.073	0.177	0.463	0.64	0.285
53a	m-Chlorotoluene	1.067	0.154	0.437	0.59	0.244
53b	"	1.067	0.155	0.475	0.63	0.227

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
54a	p-Phenoxytoluene	0.972	0.149	0.364	0.51	0.254
54b	"	0.972	0.150	0.365	0.52	0.256
55a	p-Nitrotoluene	1.072	0.141	0.444	0.59	0.210
55b	"	1.068	0.141	0.445	0.59	0.208
56a	p-Xylene	1.026	0.345	0.369	0.71	0.808
56b	"	1.026	0.329	0.368	0.70	0.765
57a	Mesitylene	0.959	0.296	0.280	0.58	0.828
57b	"	0.959	0.286	0.270	0.56	0.824
58a	Ethylbenzene	1.270	0.319	0.419	0.74	0.804
58b	"	1.270	0.337	0.429	0.77	0.838
59a	Cumene	1.162	0.375	0.390	0.77	0.957
59b	"	1.162	0.357	0.389	0.75	0.908
60a	Diphenylmethane	1.21	0.397	0.305	0.70	1.36
60b	"	1.21	0.398	0.305	0.70	1.36
60c	"	1.75	0.350	0.379	0.73	1.36
60d	"	4.45	0.246	0.565	0.81	1.51
61a	Triphenylmethane	2.51	0.417	0.262	0.68	3.48
61b	"	3.76	0.360	0.330	0.69	3.48
62a	Indan	1.916	0.519	0.285	0.80	3.12
62b	"	1.916	0.502	0.266	0.77	3.22

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
63a	Tetralin	2.13	0.554	0.227	0.78	4.70
63b	"	2.13	0.599	0.228	0.83	5.10
64a	Hexamethylbenzene	6.67	0.297	0.550	0.85	2.95
64b	"	6.65	0.302	0.501	0.80	3.30
65	Biphenyl	2.98	0.061	0.621	0.68	0.03
66	Triphenylamine	8.00	0.056	0.625	0.68	0.03
67	Diphenyl ether	1.01	0.060	0.485	0.55	0.01
68	Triphenylphosphine	4.02	<0.01	0.036	0.04	--
69a	3-Picoline	1.01	0.115	0.508	0.62	0.12
69b	"	1.01	0.100	0.519	0.62	0.09
70a	4-Picoline	1.01	0.113	0.533	0.65	0.11
70b	"	1.01	0.119	0.529	0.65	0.12
71a	s-Collidine	1.10	0.212	0.472	0.68	0.370
71b	"	1.10	0.213	0.467	0.68	0.374
72a	2,5-Dimethylpyrazine	0.575	0.181	0.224	0.41	0.326
72b	"	1.13	0.145	0.346	0.49	0.298
73a	2-Methylfuran	0.926	0.120	0.260	0.38	0.235
73b	"	0.926	0.121	0.263	0.38	0.236

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
74a	3-Methylthiophene	0.985	0.144	0.365	0.51	0.242
74b	"	0.985	0.143	0.369	0.51	0.238
75a	2-Methylthiophene	0.987	0.239	0.420	0.66	0.435
75b	"	0.987	0.234	0.407	0.64	0.436
76a	Di-2-thienylmethane	1.870	0.517	0.208	0.73	4.17
76b	"	1.862	0.526	0.211	0.74	4.19
77	Pyrrole	2.15	0.035	0.503	0.54	--
78	N-Methylpyrrole	2.30	0.082	0.360	0.44	0.3
79a	2,5-Dimethylpyrrole	1.05	0.432	0.290	0.72	1.37
79b	"	1.05	0.456	0.285	0.74	1.48
80a	Trimethylamine	0.888	0.646	0.158	0.80	3.33
80b	"	1.73	0.530	0.262	0.79	3.14
81a	N,N-Dimethylaniline	0.536	0.611	0.107	0.72	2.79
81b	"	1.067	0.543	0.171	0.71	3.04
81c	"	2.18	0.231	0.251	0.48	1.54
81d	"	5.00	0.377	0.419	0.80	3.85
82a	Thioanisole	1.795	0.163	0.512	0.68	0.384
82b	"	2.46	0.135	0.561	0.70	0.356
83a	Methanol	0.1053	0.436	0.315	0.75	0.128
83b	"	0.1397	0.410	0.361	0.77	0.138

Table 2. (Continued)

Reaction number	Compound	(CCl)	Yield^a benzene	Yield^a chloro-benzene	Total yield^a	Total reac-tivity^b
84a	Dimethyl ether	0.888	0.213	0.513	0.73	0.275
84b	"	0.888	0.209	0.505	0.71	0.272
85a	Anisole	0.510	0.134	0.437	0.57	0.093
85b	"	1.02	0.101	0.541	0.64	0.089
86a	Acetone	0.0965	0.430	0.208	0.64	0.174
86b	"	0.1520	0.395	0.289	0.68	0.179
87a	3-Pentanone	1.093	0.428	0.321	0.75	1.27
87b	"	0.880	0.475	0.280	0.76	1.32
88a	Diisopropyl ketone	2.95	0.291	0.481	0.77	1.23
88b	"	2.95	0.237	0.467	0.70	1.16
89a	Acetic acid	0.297	0.198	0.508	0.71	0.084
89b	"	0.297	0.198	0.516	0.71	0.083
90a	Methyl acetate	0.491	0.150	0.555	0.71	0.085
90b	"	0.334	0.183	0.513	0.70	0.084
91a	Methyl benzoate	0.259	0.069	0.255	0.32	0.015
91b	"	0.259	0.060	0.245	0.31	0.006
92a	Dimethyl malonate	0.475	0.235	0.472	0.71	0.182
92b	"	0.475	0.227	0.462	0.69	0.178
93a	2,4-Pentanedione	2.13	0.181	0.567	0.69	0.477
93b	"	1.777	0.202	0.565	0.71	0.465

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
94a	Isobutyronitrile	0.555	0.471	0.317	0.79	0.731
94b	"	0.555	0.458	0.307	0.77	0.730
95a	Propionitrile	0.312	0.431	0.308	0.74	0.382
95b	"	0.312	0.414	0.310	0.72	0.362
96a	Acetonitrile	0.1092	0.339	0.352	0.69	0.088
96b	"	0.1092	0.354	0.361	0.72	0.091
97a	Tetramethylsilane	0.706	0.221	0.400	0.62	0.295
97b	"	0.706	0.208	0.402	0.61	0.271
98a	Phenyltrimethylsilane	1.078	0.138	0.462	0.60	0.196
98b	"	1.078	0.140	0.457	0.60	0.203
99a	2-Nitropropane	0.560	0.258	0.467	0.73	0.244
99b	"	0.560	0.270	0.497	0.77	0.244
100a	Nitroethane	0.299	0.331	0.453	0.78	0.183
100b	"	0.299	0.335	0.454	0.79	0.185
101a	Nitromethane	0.1146	0.229	0.442	0.67	0.045
101b	"	0.1146	0.230	0.437	0.67	0.046
102a	Dimethyl sulfoxide	0.092	0.225	0.397	0.62	0.040
102b	"	0.148	0.173	0.473	0.65	0.037
103a	Trichloromethane	1.00	0.670	0.183	0.85	3.36
103b	"	0.496	0.740	0.108	0.85	3.15

Table 2. (Continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield[a] benzene	Yield[a] chlorobenzene	Total yield[a]	Total reactivity[b]
104a	Dichloromethane	0.990	0.307	0.522	0.83	0.480
104b	"	0.505	0.428	0.407	0.84	0.464
105a	Chloromethane	0.839	0.105	0.613	0.72	0.070
105b	"	0.866	0.099	0.636	0.74	0.061
106a	Diphenylsilane	1.53	0.651	0.119	0.77	7.66
106b	"	1.53	0.613	0.110	0.72	7.79
107a	Triphenylsilane	6.99	0.360	0.461	0.82	4.64
107b	"	10.00	0.302	0.514	0.82	4.83
108a	Diphenylamine	7.10	0.212	0.513	0.73	2.19
108b	"	10.00	0.186	0.567	0.75	2.32
109a	Diphenylphosphine	3.57	0.036	0.00	0.04	--
109b	"	3.57	0.061	0.00	0.06	--
109c	"	7.16	0.402	0.029	0.43	87.
109d	"	10.4	0.258	0.046	0.30	46.
110a	Acetone-d_6	0.0961	0.168	0.271	0.44	0.0404
110b	"	0.1284	0.155	0.324	0.48	0.0401
111a	Toluene-α-d_3	1.00	0.094	0.502	0.60	0.063
111b	"	0.372	0.110	0.319	0.43	0.052

Table 3. Decompositions of phenylazotriphenylmethane in single solvents at 60 °C

Solvent	Molarity of PAT	Yield[a] benzene	Yield[a] chlorobenzene
Carbon tetrachloride	0.048	0.048	0.83
" "	0.096	0.057	0.73
" "	0.144	0.072	0.68
" "	0.192	0.080	0.62
Chloroform	0.096	0.87	None
Methylene chloride	0.096	0.77	None
Methyl chloride	*ca.* 0.15	0.17	None
" "	*ca.* 0.1	0.21	None
Cyclohexane	0.047	0.85	----
Cyclopentene	0.096	0.58	----
Cyclohexene	0.097	0.72	----
Chlorobenzene	0.096	0.07	----
Trimethylchlorosilane	*ca.* 2.9	0.32	None

[a] Mole/mole PAT.

Table 4. Reactions of phenyl radicals with silicon and phosphorus chlorides

Solvent(s)	Molarity of phenyl radical source	Phenyl radical source	Yield benzene (mole/ mole Ph)	Yield chlorobenzene (mole/ mole Ph)
Silicon tetrachloride	0.097	PAT	0.70 (GPC)	0.04
" "	0.097	PAT	0.68 (GPC)	ND[a]
" "	0.097	PAT	0.77 (UV)	--
Silicon tetrachloride (17.5 mmole), cyclohexane (9.25 mmole)	0.097	PAT	0.50 (GPC)	0.04
Silicon tetrachloride (17.5 mmole), cyclohexane (9.25 mmole)	0.097	PAT	0.75 (GPC)	ND[a]
Silicon tetrachloride	0.099	Benzoyl peroxide[b]	1.31 (GPC)	0.14
Phosphorus trichloride	0.097	PAT	0.02 (?)	None
Phosphorus trichloride (11.4 mmole), cyclohexane (18.5 mmole)	0.097	PAT	None	None
Phosphorus trichloride (23 mmole), cyclohexane (9.25 mmole)	0.097	PAT	None	None
Phosphorus trichloride	0.05	Benzoyl peroxide[b]	None	None
Phosphorus trichloride	0.099	Benzoyl peroxide[b]	None	None

[a] None detected.

[b] Reactions with benzoyl peroxide were maintained at 80 °C for 72 hr.

Table 5. Influence of oxygen on yields of abstraction products during decomposition of 0.095 M PAT in carbon tetrachloride at 60 °C

Total pressure, atm.	Oxygen pressure, atm.	Yield PhCl[b]	0.74-PhCl	k_{O_2}/k_{Cl}[a] (approx.)
0.58	0.00	0.74	0.00	----
1.00	0.42	0.40	0.34	3200
2.07	1.49	0.21	0.53	2700
3.08	2.50	0.14	0.60	2700
4.10	3.52	0.09_3	0.65	3200
			Average	3000

[a] See text.

[b] Mole/mole PAT.

Table 6. Influence of oxygen on yields of abstraction products during decomposition of 0.058 M PAT in cyclohexane at 60 °C

Total pressure, atm.	Oxygen pressure, atm.	Yield PhH[b]	0.82-PhH	k_{O_2}/k_H[a] (approx.)
0.52	0.00	0.82	0.00	-----
1.00	0.48	0.48	0.34	7,100
2.07	1.55	0.16	0.66	12,600
3.08	2.56	0.12	0.70	11,000
4.10	3.58	0.07_8	0.74	12,600
			Average	10,000

[a] See text.

[b] Mole/mole PAT.

DISCUSSION

The present investigation is the first quantitative study of abstraction reactions of the phenyl radical. The results of this study constitute the most extensive list of relative reactivities (more than 100) for abstraction reactions involving organic compounds in the liquid phase to appear in the literature, in regard to both the number and types of compounds studied. This is due to the simplicity of the experimental approach and the availability in recent years of improved instrumental techniques for analyses of organic mixtures.

A comparable list of reactivities exists for the abstraction reactions of the methyl radical in the gas phase (23, 24). In 1954 the absolute rate constants for abstraction reactions of methyl radicals with about 60 organic compounds were known, and the list is only slightly larger at present due to the experimental difficulties encountered in studies of gas phase kinetics.

While absolute rate constants are desirable for theoretical reasons, relative rate constants are as useful for most purposes and are likely to be more accurate because of the experimental simplicity with which they can be obtained. In principle absolute rate constants can be calculated from relative data if the absolute rate constant is determined for one member of the series, a technique which has been used for reactions of the methyl radical.

The present work includes the first systematic investigation of abstraction reactions at side chains of alkyl-substituted heteroaromatic compounds. Past efforts have concentrated exclusively on benzene derivations.

The effects of functional groups on the reactivities of *alpha* carbon-hydrogen bonds toward radicals have been deduced previously from qualitative data. While some quantitative data are available for reactions in the gas phase of methyl radicals with functional compounds, the data reported in this thesis constitute the most comprehensive study of the effects of functional groups on reactivities of carbon-hydrogen bonds toward radicals in the liquid phase.

The present work includes one of the few quantitative studies of the reactivities of hydrogen atoms bonded to atoms other than carbon.

Further examples of the abnormally low reactivities of tertiary carbon-hydrogen bonds *beta* to tertiary or quaternary carbon atoms are provided by the present investigation.

Factors Influencing Transfer Reactions

Among the factors influencing the rates of transfer reactions of the type

$$R\cdot + R'H \longrightarrow RH + R'\cdot \qquad (19)$$

are the bond dissociation energies of RH and R'H (i.e., heat of reaction), the degree of bond breaking in the transition state, polar effects, solvent effects, and steric effects.

Discussing the rates of reactions in terms of heats of reaction or bond dissociation energies implies that a direct relationship exists between heats of reaction and energy of activation. Such a relationship was first formalized by Evans and Polanyi (25) and a linear relationship of the form (Polanyi's Rule)

$$\Delta E_a = -\alpha\Delta(\Delta H) \qquad (20)$$

involving differences of activation energies (E_a) and heats of reaction (ΔH) has been found a reasonable approximation for many systems. The constant, α, can vary between zero and unity and is generally taken as a measure of the extent of bond breaking in the transition state, and as a measure of the reactivity of the attacking radical (26). Inspection of Equation 20 shows that a smaller value of α will result in a lower value of the activation energy for a particular value of the heat of reaction.

In comparing the relative reactivities of a series of compounds (R_2H, R_3H, etc.) toward a single radical ($R\cdot$) it is frequent practice to discuss reactivities in terms of bond dissociation energies (BDE), since the heats of reactions are given by: BDE(RH) - BDE(R_2H), BDE(RH) - BDE(R_3H), etc., where BDE(RH) is constant throughout the series. Because so many bond dissociation energies of interest are not known it is customary to discuss reactivities qualitatively in terms of the relative stabilities of the radicals resulting as products of abstraction reactions. While this point of view is not entirely accurate, it is useful when comparing reactivities of similar compounds and will be used frequently in this section.

The influence of polar contributions to the transition state has been discussed by Russell (27, 28), who demonstrated that electron availability at the carbon-hydrogen bond undergoing attack strongly influences reaction rates of radicals with high electron affinities. In the case of an electron deficient radical, the contribution of resonance form II to the transition state is substantial:

$$\underset{\text{I}}{\mathrm{R{:}H{\cdot}X}} \longleftrightarrow \underset{\text{II}}{\mathrm{R^{+}{\cdot}H^{-}{:}X}} \longleftrightarrow \underset{\text{III}}{\mathrm{R{\cdot}H{:}X}}. \qquad (21)$$

For reasons discussed earlier (Literature Review) polar effects are expected to be unimportant in reactions of the phenyl radical.

While free radical reactions are usually conducted in non-polar solvents, the influence of the reaction medium has generally been presumed to be relatively unimportant until recently. Studies of chlorination (29) in a wide variety of solvents have revealed that certain classes of compounds, especially aromatics, have the ability to complex with an atom or free radical and greatly decrease its selectivity. In view of the profound solvent effect recently reported by Walling and Padwa (30) for a bulky alkoxy radical, some consideration must be given to this factor in a discussion of reactions of the phenyl radical.

Among steric effects in abstraction reactions may be considered the hindrance offered by bulky groups to the approach of the alkyl radical and the effect of such groups on the stability of the product radical. Steric inhibition of resonance (31) becomes important in reactions of substituted benzenes. The relative stabilities of cycloalkyl radicals are generally interpreted in terms of the effects of ring strain (32, 33).

Since the driving force of Reaction 19 is provided mainly by the bond dissociation energy of the newly formed carbon-hydrogen bond in RH, the reactivities of different radicals toward the same compound (or same series of compounds) can be predicted to a first approximation by the dissociation energies of the bonds involved. Szwarc and Binks (34) have applied such arguments on a semi-quantitative basis to obtain the correct order of reactivity for three alkyl radicals: methyl > ethyl > _n_-propyl. The bond dissociation energy (35) of methane is well established at 101 - 102 kcal/mole. Benzene has a carbon-hydrogen bond dissociation energy of 102 kcal/mole, with an upper limit of 107 kcal/mole. From these considerations the reactivity of the phenyl radical is predicted to be greater than or equal to that of the methyl radical.

Alkanes

Solution of the simultaneous equations from the total reactivities of model alkanes toward phenyl radicals yielded values of 0.038, 0.36, and 1.78 (ratios 1:9.5:47), respectively, for the reactivities of primary, secondary, and tertiary carbon-hydrogen bonds. The model compounds chosen for the calculations of primary and secondary reactivities were the normal alkanes. Tertiary carbon-hydrogen reactivities were calculated from alkanes having only one branching group. The value of k_H/k_{Cl} calculated for neopentane and tetramethylbutane is 0.045, or 18% higher than the primary reactivity obtained from the normal alkanes. This is consistent with the bond dissociation energies (35), the value for neopentane being 4 - 6 kcal/mole lower than the values reported for the primary carbon-hydrogen bonds of normal alkanes. (A general discussion of the dependence of reactivities upon bond dissociation energies will be postponed until the end of this section.)

The average reactivity of a secondary paraffinic carbon-hydrogen bond was calculated by solving the simultaneous equations for the reactivities of pentane, hexane, and heptane. All three combinations of equations were solved to give a value of k_H/k_{Cl} for the secondary carbon-hydrogen bond of 0.36 ± 0.05. This value was substituted in the original equations in order to calculate the contribution of the methyl groups. (Because the same number of methyl groups are present in each normal alkane, these terms disappeared when the equations were solved for the secondary carbon-hydrogen bond reactivity.) The average value so obtained for the primary aliphatic carbon-hydrogen bond was 0.038 ± 0.003. By substituting these values in the equations for the reactivities of 3-methylpentane and 3-methylhexane two values were obtained for the reactivity of the tertiary carbon-hydrogen bond. The average was 1.78 ± 0.01. The objective was not to get the best possible fit for all the data, but to obtain representative values for the individual bond reactivities of the simplest paraffins in order to discern anomalies. Application of this procedure to more complicated alkanes resulted in physically impossible values.

A comparison (Table 7) of the selectivities of various radicals toward alkanes reveals close similarities in the reactivities of primary, secondary, and tertiary carbon-hydrogen bonds toward the phenyl, methyl, and t-butoxy radicals. The extremely reactive chlorine atom demands a very low energy of activation (26) in its abstraction reactions which is reflected in its selectivity, the ratio k(tert.)/k(prim.) being one-tenth of that observed for the other three radicals.

In Table 7 the reactivities of eighteen alkanes have been calculated using the relative rate constants of 0.038, 0.36, and 1.78 for primary, secondary, and tertiary carbon-hydrogen bonds, respectively. A value of 0.045 was used for each carbon-hydrogen bond of dimethylpropane and tetramethylbutane. The agreement between the experimental and calculated values is quite good for the simpler compounds and becomes rather poor for certain highly branched hydrocarbons.

Close inspection of Table 7 reveals that the reactivity of a tertiary carbon-hydrogen bond <u>beta</u> to a quaternary or tertiary carbon atom is abnormally low. This can be developed by considering the reactivities of six compounds in detail. The reactivity of 2,3-dimethylbutane is slightly higher than predicted while 2,5-dimethylpentane is only 56% as reactive as predicted. This low reactivity must be attributed to the tertiary carbon-bonds in 2,5-dimethylpentane and not to low reactivity of the central methylene group because the <u>total</u> reactivity of 2,5-dimethylpentane is less than that of 2,3-dimethylbutane (e.g., less than if the methylene group were

Table 7. Reactivities of alkanes toward the phenyl radical at 60 °C

Alkane	Experimental reactivity[a]	Calculated reactivity[b]	$\frac{\text{Experimental}}{\text{Calculated}}$
Dimethylpropane	0.135	0.135	1.00
Tetramethylbutane	0.203	0.202	1.01
Pentane[c]	0.59	0.60	0.99
Hexane[c]	0.79	0.78	1.01
Heptane[c]	0.95	0.96	0.99
Octane	1.13	1.14	0.99
Hexadecane	2.51	2.58	0.97
2,2-Dimethylbutane	0.29	0.29	1.00
3-Methylpentane[c]	0.89	0.89	1.00
2-Methylpentane	0.86	0.89	0.97
3-Methylhexane[c]	1.07	1.07	1.00
2,3-Dimethylbutane	1.17	1.00	1.17
2,4-Dimethylpentane	0.66	1.18	0.56
2,5-Dimethylhexane	1.27	1.36	0.93
2,2,3-Trimethylbutane	0.71	0.59	1.20
2,2,4-Trimethylpentane	0.35	0.77	0.45

[a] Experimental reactivity $= \frac{(CCl_4)(PhH-0.054)}{(R\dot{H})(PhCl)}$.

[b] Calculated reactivity $= \frac{\Sigma n_i k_{i(H)}}{4k_{(Cl)}}$.

[c] Model compounds.

Table 7. (Continued)

Alkane	Experimental reactivity[a]	Calculated reactivity[b]	$\frac{\text{Experimental}}{\text{Calculated}}$
2,2,5-Trimethylhexane	0.81	0.95	0.85
2,3,4-Trimethylpentane	0.96	1.47	0.67

zero). Furthermore the reactivity of 2,5-dimethylhexane, in which the tertiary carbon-hydrogen bonds are separated by two methylene groups is 93% as reactive as the predicted value.

The same arguments apply with greater force to the case of isooctane (2,2,4-trimethylpentane). This paraffin is only 45% as reactive as predicted, while its next lower homologue, triptane (2,2,3-trimethylbutane), has a reactivity 20% higher than the predicted value. The higher homologue, 2,2,5-trimethylhexane, is 85% as reactive as predicted. Since the total reactivity of isooctane is about half that of triptane, this anomaly cannot be ascribed to the methylene group of isooctane. (Assigning the methylene group zero reactivity and all other carbon-hydrogen bonds "normal" reactivities leads to the prediction that triptane and isooctane should have equal reactivities.) Assigning both the primary and secondary carbon-hydrogen bonds values of zero (k_H/k_{Cl}) leads to a predicted value for the reactivity of isooctane of 0.45, which is still larger than the observed value. If the tertiary carbon-hydrogen bond of isooctane is assigned a reactivity of zero, the calculated total reactivity becomes 0.33 which compares well with the experimental value of 0.35. Indirect evidence for the low reactivity of the tertiary carbon-hydrogen bond of isooctane is offered by the rate (36) and products (37) of high temperature oxidation, and by the addition to naphthalene of radicals derived from isooctane (38).

The examples discussed above indicate that a tertiary hydrogen attached to a carbon which is *beta* to a quaternary or tertiary carbon atom is abnormally unreactive with regard to abstraction by a free radical. The same conclusion was reached by Brook (39) during a study of the t-butoxy radical. Brook noted the low reactivities of 2,4-dimethylpentane and isooctane, and observed the same reactivity pattern in the cyclohexyl series. The relative reactivities per molecule toward the t-butoxy radical of dicyclohexyl (1.00), dicyclohexylmethane (0.89), and 1,2-dicyclohexylethane (1.25) follow the same order as the acyclic analogues.

The following explanation was offered by Brook. Examination of molecular models indicates that the preferred conformation of 2,3-dimethylbutane is that in which the two tertiary carbon-hydrogen bonds are *trans* to each other, while the most strain-free conformer of 2,4-dimethylpentane is that in which the two tertiary hydrogens are in a *cis*

Table 8. Comparison of selectivities of various radicals toward alkanes

Type of bond	Phenyl 60°	Methyl[a] 182° (gas)	t-Butoxy[b] 40°	Chlorine[c] 25°
Prim.	(1),[d] 1.2	(1)[d]	(1)[d]	(1)[d]
Sec.	9.5	7	8, 12	3.6
Tert.	47	50	44	4.2

[a] Reference 23.

[b] Reference 40.

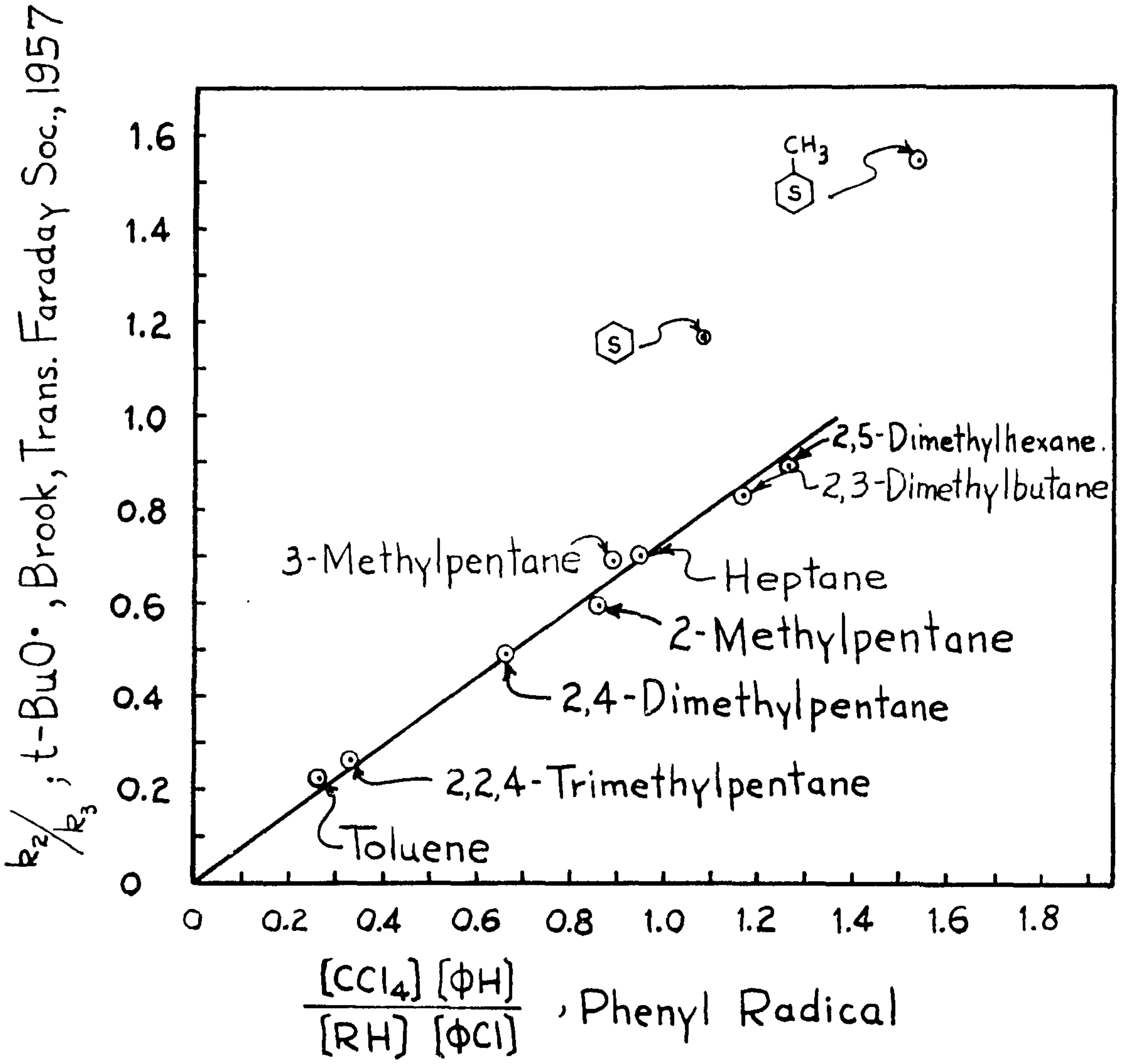
[c] Reference 29.

[d] Assumed.

position, with the hydrogen atoms nearly in contact. In such a conformer of 2,4-dimethylpentane the tertiary carbon-hydrogen bonds are relatively inaccessible to a bulky radical such as t-butoxy or phenyl.

A comparison of the reactivities of alkanes toward the t-butoxy and phenyl radicals appears in Figure 2. The two sets of data agree exceptionally well in the acyclic series, but the cyclic alkanes are conspicuous in their greater reactivities toward the t-butoxy radical. The value given by Brook for cyclohexane is lower than those obtained by two other groups of workers (40, 41). No explanation is

Figure 2. Comparison of the relative reactivities of alkanes toward t-butoxy and phenyl radicals


k_2/k_3 ; t-BuO• , Brook, Trans. Faraday Soc., 1957
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
$\frac{[CCl_4]\,[\phi H]}{[RH]\,[\phi Cl]}$, Phenyl Radical
Toluene
2,2,4-Trimethylpentane
2,4-Dimethylpentane
2-Methylpentane
3-Methylpentane
Heptane
2,3-Dimethylbutane
2,5-Dimethylhexane.
S
CH3
S

offered for the higher reactivity of cyclic alkanes toward the t-butoxy radical. It is interesting to note that data (23, 24, 42) for the methyl radical in the vapor phase show the reactivities of cyclic alkanes (viz., cyclopentane and cyclohexane) to be about the same as those of normal paraffins containing the same number of methylene groups. Such is the case in the present work. A detailed comparison of the methyl and phenyl radicals appears later in this section.

Reactions of the phenyl radical with cyclic alkanes demonstrate the pattern expected from steric considerations (29, 32). The reactivities are in accord with the stabilities of the resulting cycloalkyl radicals (33). A comparison with other radicals is presented in Table 9.

Solvent Effects

The abilities of certain solvents, especially aromatic compounds, to form π-complexes with free radicals have been aptly demonstrated (20, 29, 43). The result of such interaction is a decrease in reactivity of the radical in the complexed form. In reactions of the chlorine atom the influence of solvent is large and has been quantitatively explained (29) in terms of dissociation constants of the complexes.

Before attempting a study of the reactions of more complex compounds with the phenyl radical it was necessary

Table 9. Comparison of reactivities per bond of cyclic alkanes toward various radicals

Cyclic alkane	Phenyl 60°	Chlorine[a] in 4M t-butylbenzene 40°	Methyl-d_3[b] 60° (gas)	t-Butoxy[c] 68°
Cyclooctane	2.00	2.3	---	---
Cycloheptane	1.80	1.5	2.2	---
Cyclopentane	1.15	1.1	1.3	0.90
Cyclohexane	(1)[d]	(1)[d]	(1)[d]	(1)[d]
Methyl-cyclopentane[e]	3°, 1.08	---	---	
Methyl-cyclohexane[f]	3°, (1)[d]	---	---	

[a] Reference 29.

[b] Reference 42.

[c] Reference 40.

[d] Assumed.

[e] Tertiary, $$\frac{k_H}{k_{Cl}} = 4(1.525) - 3(0.038) - 8(0.416)$$

$$= 2.66.$$

[f] Tertiary, $$\frac{k_H}{k_{Cl}} = 4(1.54) - 3(0.038) - 10(0.36)$$

$$= 2.45.$$

to determine whether strong solvent effects were likely to be operative, especially in the aromatic series. Since the formation of a π-complex between a radical and an aromatic solvent is dependent upon the concentration of the aromatic compound, one approach is to determine whether the rate constant for a particular reaction is dependent upon concentration. As shown in Table 1 the relative rate constant for the abstraction of the benzylic hydrogen of toluene by the phenyl radical is independent of toluene concentration, indicating no strong solvent effect. Further examples of varying the concentration of the hydrogen-containing substrate over approximately a two-fold range may be found in Table 2. Variation of the concentration of aromatic compounds, compounds containing functional groups, and compounds containing hydrogen bonded to heteroatoms showed no significant dependency of the relative rate constants upon concentration.

The effect of adding aromatic solvents to an alkane was investigated in the case of cyclohexane. The decomposition at 60 °C of 0.1 M PAT in a solution of 4.2 M carbon tetrachloride, 4.3 M cyclohexane, and 1.15 M nitrobenzene gave a value for k_H/k_{Cl} of 0.34 ± 0.02, with a decrease in the total yield of abstraction products of 7.3% attributable to the presence of the aromatic solvent. A similar experiment using 1.46 M pyridine with the same molarities of carbon tetrachloride and cyclohexane yielded a value of 0.33 ± 0.02

for k_H/k_{Cl}, with a yield decrease of 6.6%. The value of k_H/k_{Cl} in the absence of added aromatic solvents is 0.36.

In the present work no solvent effects were observed, but the possibility that relative rate constants change with concentration in extremely dilute mixtures not amenable to the employed experimental techniques cannot be excluded. Walling and Padwa (30) recently observed that the benzyldimethylmethoxy radical in the presence of small amounts of cyclohexene reacts exclusively by decomposing, and no hydrogen abstraction takes place. These same authors suggested the need for caution in interpreting the results of competitive reactions involving olefins and alkoxy radicals.

Alkenes and Alkynes

The relative reactivities of primary, secondary, and tertiary allylic carbon-hydrogen bonds toward the phenyl radical at 60 °C were calculated to be (k_H/k_{Cl}) 0.57, 1.11, and 4.77 respectively. In computing these values, all carbon-hydrogen bonds were taken into account with the exception of those bonded to the olefinic carbon, which were assigned a value of zero reactivity. The values given above are average values and, as shown in Table 10, predict the reactivities of several compounds within values of about 30% of the experimental value.

Table 10. Reactivities of alkenes and alkynes toward the phenyl radical at 60 °C

Alkene	Experimental reactivity[a]	Calculated reactivity[b]	Experimental / Calculated
cis-2-Butene[c]	0.86	0.86	1.00
trans-2-Butene[c]	0.62	0.86	0.72
2-Methyl-2-butene[c]	1.22	1.28	0.95
2,3-Dimethyl-2-butene[c]	2.25	1.71	1.31
1-Butene[c]	0.63	0.59	1.08
1-Pentene[c]	0.71	0.77	0.93
2-Pentene	1.28	1.01	1.27
1-Octene[c]	1.31	1.31	1.00
2-Octene	1.58	1.55	1.02
2-Methyl-1-butene	0.88	1.01	0.87
3-Methyl-1-butene[c]	1.42	1.26	1.13
4-Methyl-2-pentene[c]	1.46	1.67	0.87
2,5-Dimethyl-2,4-hexadiene	2.94	----	----
Propyne	0.27	----	----
1-Butyne	0.98	----	----

[a] Experimental reactivity $= \frac{(CCl_4)(PhH-0.054)}{(RH)(PhCl)}$.

[b] Calculated reactivity $= \frac{\Sigma n_i k_{i(H)}}{4k_{(Cl)}}$.

[c] Model compounds.

Table 10. (Continued)

Alkene	Experimental reactivity[a]	Calculated reactivity[b]	Experimental / Calculated
2-Butyne	0.87	----	----
Allylbenzene	1.80	----	----
Cyclopentene	3.56	----	----
Cyclohexene	4.33	----	----

The calculations of reactivities per bond for the olefinic series were similar to those described previously for the alkanes. All non-allylic carbon-hydrogen bonds were assigned relative reactivities (k_H/k_{Cl}) of 0.038, 0.36, and 1.78 for primary, secondary, and tertiary, respectively. Model alkanes for the reactivity of the primary allylic carbon-hydrogen bond were *cis*- and *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene, which yielded an average value for the allylic primary k_H/k_{Cl} of 0.57 ± 0.18. Model compounds for the reactivity of the secondary allylic carbon-hydrogen bond were 1-butene, 1-pentene, and 1-octene; the average secondary allylic k_H/k_{Cl} was 1.11 ± 0.1. Model compounds for the tertiary allylic bond were 4-methyl-2-pentene and 3-methyl-1-butene, which gave an average value of 4.77 ± 0.85 for the relative reactivity of a tertiary allylic carbon-hydrogen bond. In calculating the reactivities per bond of cyclic olefins the k_H/k_{Cl} values of the corresponding cyclic alkanes were assigned to non-allylic carbon-hydrogen bonds.

Walling and Thaler (40) have maintained that the reactivity of an allylic carbon-hydrogen bond depends not only upon the substitution at the site of attack, but also the degree of substitution at the *beta* carbon which bears the free electron in resonance structures of the radical formed from the abstraction reaction. Thus there should be three types each of primary, secondary, and tertiary allylic reactivities, resulting in nine different allylic reactivities. The operation of steric factors makes the assignment of reactivities to individual bonds in olefins an even more approximate practice. In view of these considerations, agreement between the experimental and calculated values of within 30% is not considered a large deviation. The data obtained in the present study do not permit the separation of the factors considered above.

Investigations of the reactivities of olefins with different radicals often given conflicting results. The reactivities of *cis*- and *trans*-2-butene are a case in point. From the present study the reactivity of *cis*-2-butene toward abstraction by a phenyl radical is 1.38 times as great as that of *trans*-2-butene. This agrees qualitatively with the relative rates of abstraction by the t-butoxy radical (40) at 40°, the *cis* isomer reacting 1.06 times faster than the *trans*. On the other hand Buckley and Szwarc (44) found abstraction by methyl radicals at 65° to proceed 1.53 times faster with the *trans* isomer. Explanations have been offered for specific examples, but no generalization seems to cover these three cases. The rates of addition of these three radicals to *cis*- and *trans*-2-butene present an equally confusing picture (see below).

A comparison of the reactivities of allylic carbon-hydrogen bonds toward three different radicals is given in Table 11. Considering that the reactivities in Table 11 are average values, the agreement is fairly good. The higher selectivity of the methyl radical in the liquid phase is not understood.

Table 11. Comparison of reactivities of allylic carbon-hydrogen bonds toward various radicals

Type of bond	Phenyl 60 °C	Methyl[a] 182° (gas)	Methyl[b] 65° (liquid)	t-Butoxy[c] 40°
Prim.	(1)[d]	(1)[d]	(1)[d]	(1)[d]
Sec.	2	3.4	10.6	4.7
Tert.	8.4	10.6	44	11

[a] Reference 23.

[b] Reference 44.

[c] Reference 40.

[d] Assumed.

A comparison of the relative reactivities of cyclohexene and cyclopentene toward several radicals is given in Table 12. It is noted that the phenyl radical provides the only example in which cyclohexene is more reactive than cyclopentene. Szwarc (45) commented on the low reactivity of cyclohexene in both addition and abstraction reactions but offered no explanation. It is of interest to compare the reactivities of cyclohexene relative to toluene in the cases of the t-butoxy and phenyl radicals. The allylic carbon-hydrogen bond in cyclohexene (40) is 36.4 times more reactive than toluene toward the t-butoxy radical at 40°. The reactivity per bond of cyclohexene relative to toluene in the present work is 11.

Table 12. Comparison of the relative reactivities per bond of cycloalkenes toward several radicals

Cycloalkene	Phenyl 60°	t-Butoxy[a] 40°	Methyl[b] 65°	NBS[c] 40°	Peroxy[d] 60°
Cyclopentene	0.84	1.04	5.4	4.8	1.57
Cyclohexene	(1)[e]	(1)[e]	(1)[e]	(1)[e]	(1)[e]

[a] Reference 40.

[b] Reference 45.

[c] Reference 46.

[d] Reference 43.

[e] Assumed.

The reactivity of the benzylic carbon-hydrogen bond of allylbenzene is 3.58 (k_H/k_{Cl}), which is slightly greater than the sum of the α-carbon-hydrogen bond of ethylbenzene (1.59) and a secondary allylic carbon-hydrogen bond (1.11). The only diene studied which was resistant enough to addition reactions that its abstraction reactivity could be measured was 2,5-dimethyl-2,4-hexadiene. Its reactivity per bond toward the phenyl radical at 60° is 0.98. Comparing this with the value of 0.75 for k_H/k_{Cl} of 2,3-dimethyl-2-butene shows that the second double bond increases the reactivity by about 30%.

Primary and secondary carbon-hydrogen bonds adjacent to an acetylenic group were found to be respectively 15.3 and 50.5 times as reactive toward the phenyl radical as a primary carbon-hydrogen bond in an alkane. The corresponding values (23) for reactions with the methyl radical at 182° are 23 and 126.

Examination of Table 2 shows that the yields are generally low for olefins. It was mentioned earlier that the addition of phenyl radicals to some olefins took place readily enough to reduce the yield of benzene below the blank correction factor. With the data at hand it is possible to make rough estimates of the relative rates of addition (k_a) of phenyl radicals to olefins. The symbols used below are defined in the preceding section.

$$RH + Ph\cdot \xrightarrow{\Sigma n_i k_{i(H)}} R\cdot + PhH \tag{22}$$

$$CCl_4 + Ph\cdot \xrightarrow{4k_{(Cl)}} Cl_3C\cdot + PhCl \tag{23}$$

$$RH + Ph\cdot \xrightarrow{k_a} A.P.\ (\text{Addition Product}) \tag{24}$$

Using the same approximations discussed in the previous section, one obtains:

$$\frac{k_a}{4k_{(Cl)}} = \frac{(CCl_4)}{(RH)} \cdot \frac{(A.P.)}{(PhCl)} \quad . \tag{25}$$

Since (A.P.) was not determined it is necessary to estimate this quantity from the decrease in yield from some standard value. The standard value of 0.763 mole/mole PAT was chosen for the following reasons. The yields of chlorobenzene and benzene from a carbon tetrachloride solution of 0.1 M PAT are 0.739 and 0.054 mole/mole PAT, respectively. Of the total yield (0.792) of abstraction products, 0.03 mole benzene/mole PAT is attributed to a cage reaction as discussed in the previous section (see Figure 1). Examination of the data of Table 2 shows that terminal olefins which are reactive toward addition of a phenyl radical cannot compete for this "cage" benzene. Subtraction of 0.03 from 0.793 gives the standard value of 0.763 mole/mole PAT for the expected total yield of abstraction products. This value is about the average of the total yields obtained during the study of alkanes. By setting (A.P.) equal to the difference between 0.763 and the total yield observed for an olefin the reactivity expression becomes:

$$\frac{k_a}{4k_{(Cl)}} = \frac{(CCl_4)}{(RH)} \cdot \frac{(0.763 - \text{total yield})}{(PhCl)} \quad . \qquad (26)$$

The quantity $k_a/4k_{(Cl)}$ is defined as the relative rate of addition of phenyl radicals to the substrate RH. The values so calculated are relative to the rate of chlorine abstraction in a molecule of carbon tetrachloride. Since the separation of these values into components for the reactivities at individual sites in the molecules is an obscure process, they have been left in this form. Relative reactivities of addition to a phenyl radical are listed in Table 13. Since the experiments of the present study were not designed with this purpose in mind, such addition reactivities are quite approximate.

A comparison of the reactivities of alkenes toward addition reactions of several radicals appears in Table 14. The agreement among the phenyl, methyl, and trichloromethyl radicals is qualitative at best. The greater selectivity of the methyl radical as compared with the phenyl radical is not understood and seems inconsistent with the observation that methyl (48) and phenyl (49) radicals add to functionally

Table 13. Relative rates of addition of phenyl radicals to olefins at 60 °C

Olefin	Approx. $\frac{k_a}{4k_{Cl}}$ (addition)	$\frac{\Sigma n_i k_{i(H)}}{4k_{Cl}}$ (abstraction)	$\frac{k_a}{\Sigma n_i k_{i(H)}}$ (addn./abstr.)
<u>cis</u>-2-Butene	1.10	0.855	1.29
<u>trans</u>-2-Butene	1.28	0.619	2.07
2-Methyl-2-butene	1.39	1.22	1.14
2,3-Dimethyl-2-butene	0.33	2.25	0.15
1-Butene	2.42	0.634	3.82
1-Pentene	2.72	0.711	3.82
2-Pentene	0.67	1.28	0.52
1-Octene	2.88	1.31	2.20
2-Octene	1.72	1.58	1.09
2-Methyl-1-butene	5.13	0.879	5.84
3-Methyl-1-butene	2.48	1.42	1.75
4-Methyl-2-pentene	0.282	1.46	0.19
Propene	1.99	----	Large
2,3,3-Trimethyl-1-butene	5.8	----	"

Table 13. (Continued)

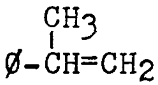
Olefin	Approx. $\frac{k_a}{4k_{Cl}}$ (addition)	$\frac{\Sigma n_i k_{i(H)}}{4k_{Cl}}$ (abstraction)	$\frac{k_a}{\Sigma n_i k_{i(H)}}$ (addn./abstr.)
3,3-Dimethyl-1-butene	2.56	----	Large
1,3-Pentadiene	24.4	----	"
2-Phenylpropene  $\text{Ø-}\overset{\text{CH}_3}{\overset{\vert}{\text{C}}}\text{=CH}_2$	14.1	----	"
1-Phenylpropene Ø-CH=CH-CH_3	5.92	----	"
3-Phenylpropene $\text{Ø-CH}_2\text{-CH=CH}_2$	2.72	1.80	1.51
Cyclopentene	1.09	3.56	3.06
Cyclohexene	0.2	4.33	0.05
2,5-Dimethyl-2,4-hexadiene	3.12	2.94	1.06
Propyne	1.13	0.27	4.18
1-Butyne	1.03	0.98	1.05
2-Butyne	0.15	0.87	0.17

Table 14. Comparison of reactivities of alkenes toward addition reactions of several radicals

Alkene	Phenyl 60°	Methyl[a] 65°	t-Butoxy[b] 40°	Trichloromethyl[c] *ca.* 60°
cis-2-Butene	(1)[d]	(1)[d]	(1)[d]	---
trans-2-Butene	1.15	1.76	0.17	---
2-Methyl-2-butene	1.26	1.47	----	---
1-Phenylpropene	5.4	16	----	3.2
3-Phenylpropene	2.47	----	----	2.0
1-Butene	2.2	7.1	0.16	---
1-Pentene	2.48	6.4	----	---
1-Octene	2.88	---	----	(2.88)[d]
3-Methyl-1-butene	2.25	6.0	0.18	---
2-Methyl-1-butene	4.66	---	----	2.6
Cyclopentene	1.0	1.53	----	2.3
Cyclohexene	0.2	0.24	----	0.3

[a] Reference 34, p. 271.

[b] Reference 40.

[c] Reference 47, p. 254.

[d] Assumed.

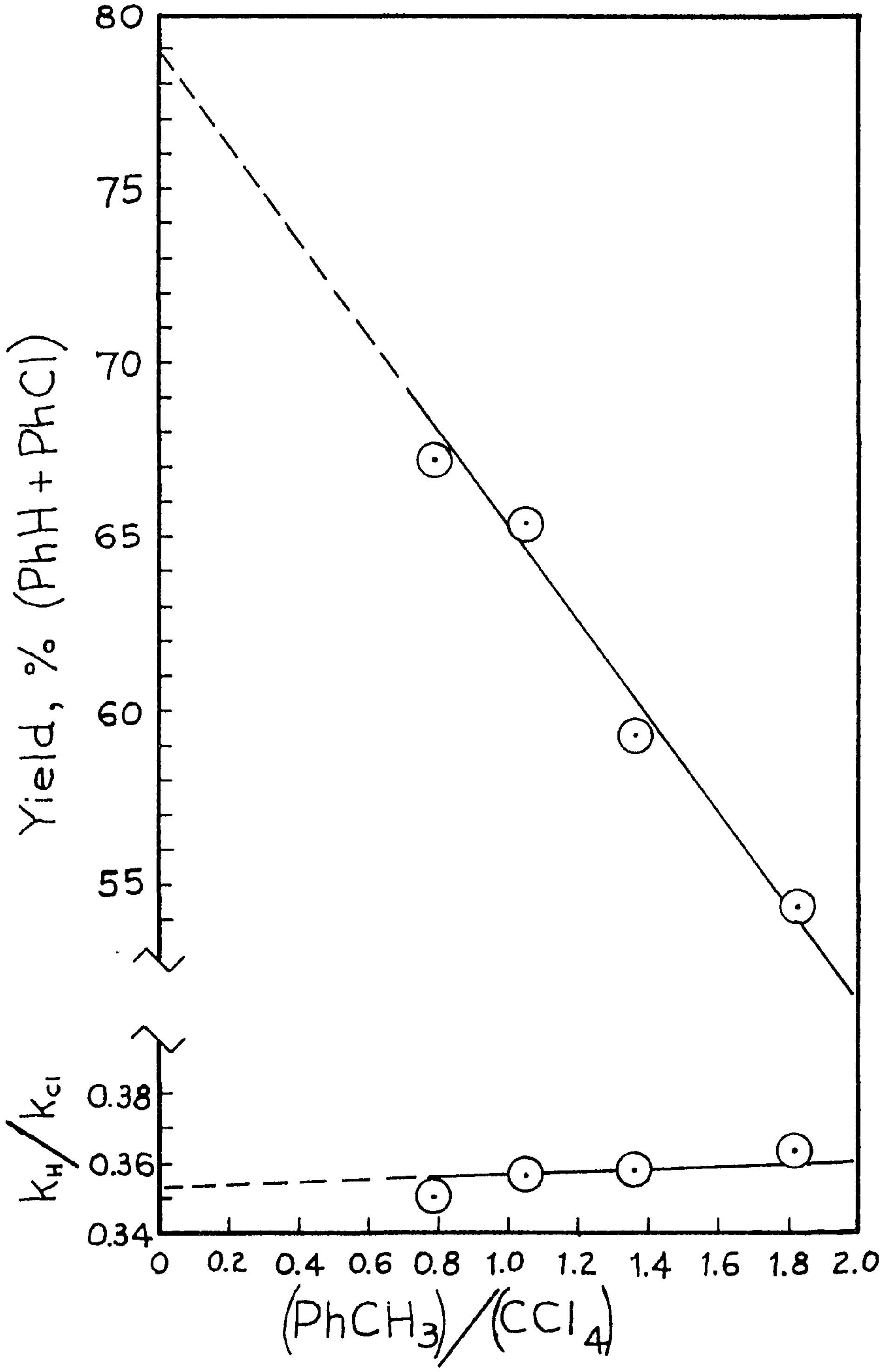
substituted olefins with the same selectivity. Particular note is taken of the agreement for the pair cyclohexene-cyclopentene in Table 14.

Aromatic Hydrocarbons

A graphical summary of the study of abstraction reactions by the phenyl radical occurring at the side chain of toluene is shown in Figure 3. It is apparent from this figure that abstraction reactions compete fairly well with homolytic arylation. During the decomposition of 0.1 M PAT in an equimolar solution of toluene and carbon tetrachloride at 60°, over 62% of the phenyl radicals may be accounted for by the total yield of abstraction products. The total yields of abstraction products from the toluene-carbon tetrachloride reactions extrapolate to 79% at zero toluene concentration, which, after application of the -5.4% correction (discussed above) gives a value of 73.6%, in good agreement with the yield of chlorobenzene (73.9%) obtained by the decomposition of 0.1 M PAT in pure carbon tetrachloride.

In calculating reactivities per bond of aralkyl hydrocarbons, all carbon-hydrogen bonds have been taken into account with the exception that hydrogen atoms attached to aromatic rings were assigned reactivities of zero. (The justification for this was discussed previously.) All non-

Figure 3. Competetive reactions of 0.096 M phenylazotriphenylmethane with toluene and carbon tetrachloride at 60 °C


80
75
70
65
60
55
Yield, % (PhH + PhCl)
0.38
0.36
0.34
k_H/k_{Cl}
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
(PhCH$_3$)/(CCl$_4$)

benzylic carbon-hydrogen bonds were assigned reactivities equal to those of the paraffinic analogues. The *beta* carbon-hydrogen bonds in tetralin and indan were assigned the same per bond reactivities as in cyclohexane and cyclopentane respectively. These approximations have but slight effect on the final relative values of reactivity. If the non-benzylic bonds are taken into account, tetralin is found to be 1.54 times as reactive as indan. Ignoring the contributions of *beta* carbon-hydrogen bonds results in a value of 1.55 for the same quantity. Primary carbon-hydrogen bonds *beta* to an aromatic ring were assigned values of 0.038 (k_H/k_{Cl}) per bond. This agrees well with the value of 0.035 obtained from t-butylbenzene.

The application of the Hammett equation to the reactivities of substituted toluenes is summarized in Figure 4. The values of σ are those of Jaffé (50), and the slope gives a value of *ca*. -0.1 for ρ, indicating the unimportance of polar contributions (27, 28) to the transition state during abstraction reactions of phenyl radicals. p-Xylene was not included in the Hammett plot; the reactivity of this compound is apparently governed by its lower bond dissociation energy (35).

A comparison of the relative reactivities of several aromatic hydrocarbons toward five radicals appears in Table 15. Since the data for all five radicals were obtained in

Figure 4. Hammett plot for reactions of phenyl radicals with substituted toluenes at 60 °C

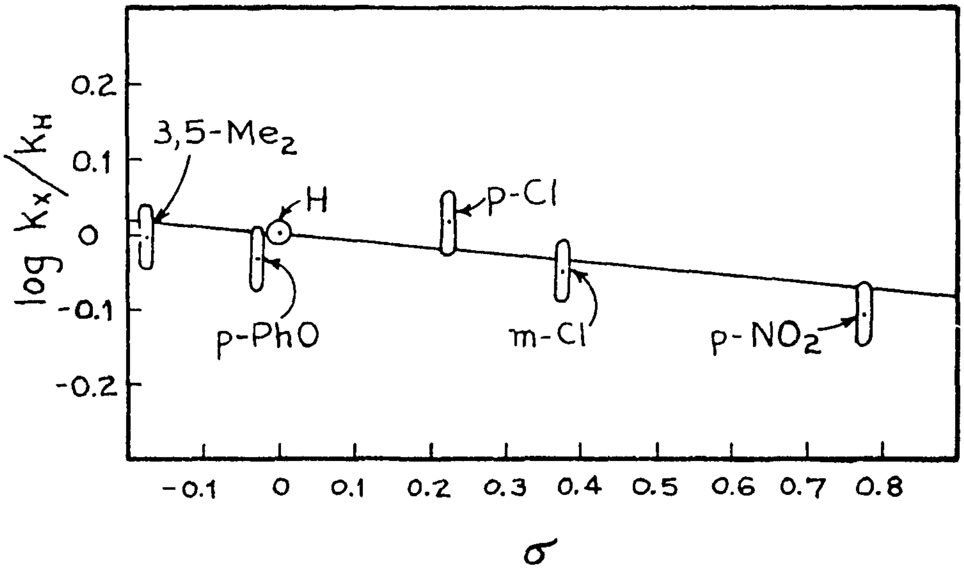

log kx/kH
0.2
0.1
0
-0.1
-0.2
3,5-Me2
H
p-Cl
p-PhO
m-Cl
p-NO2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
σ

Table 15. Relative reactivities of aralkyl hydrocarbons toward several radicals

Compound	Phenyl 60°	Methyl[a] 65°	t-Butoxy[b] 40°	Peroxy[c] 90°	Chlorine[d] 40°
Toluene	(1)[e]	(1)[e]	(1)[e]	(1)[e]	(1)[e]
Ethylbenzene	4.42	4.14	3.18	7.8	2.5
Cumene	9.78	12.9	6.84	13.3	5.5
Diphenylmethane	7.55	----	4.70	16	2.0
Triphenylmethane	38.7	----	9.60	---	7.2
p-Xylene	1.46	1.19	1.53	1.6	---
Mesitylene	1.01	0.94	1.34	1.9	---
Indan	8.2	8.3		37	4.4
Tetralin	12.6	11.5	7.6[f]	67	4.1

[a] Reference 51.

[b] Reference 52.

[c] Reference 27.

[d] Reference 43, values extrapolated to infinite dilution.

[e] Assumed; all reactivities per α-carbon-hydrogen bond.

[f] At 135 °C, Reference 41.

the liquid phase and temperature differences are not large, a comparison of selectivities based on this table should be valid. The following order of decreasing selectivity in abstraction reactions is observed for the five radicals: peroxy > methyl ≥ phenyl > t-butoxy > chlorine. This is the order of selectivities between cumene and toluene and is approximately the same for most hydrocarbons compared in Table 15. The order between methyl radical and phenyl radical is reversed in several instances, but the two radicals exhibit such similar reactivities in the aromatic series that it is questionable that the differences are greater than the combined experimental errors of the two investigations. In the above sequence the phenyl radical has been placed in a position of lower selectivity than the methyl radical because of the reactivity patterns exhibited for the olefins in Table 11.

Eliel and co-workers (9) have proposed that homolytic arylation by phenylazotriphenylmethane is a concerted homolytic process. Eliel suggested that homolytic phenylation with PAT involves an activation energy of zero, based on the observations that no dihydrobiphenyl is formed during phenylation with PAT and that the decomposition of PAT in benzene solution with added dihydrobiphenyl resulted in the consumption of only 25% of the dihydrobiphenyl. Further arguments of Eliel are based upon isotope effects observed for the removal of hydrogen from the phenylcyclohexadienyl radical (Equation 2) by a variety of radicals from different phenyl radical sources. The present study shows that, regardless of the mechanism of arylation, abstraction reactions compete quite effectively with phenylation. Furthermore, the effect of structure upon reactivity suggests definite activation energies for the abstraction reactions. This is inconsistent with Eliel's conclusions. While experimental details of Eliel's work have not been published, it is suggested here that most of his results with PAT can be interpreted in terms of the significant concentration of trityl radicals present in solution, which can oxidize (Equation 2) the phenylcyclohexadienyl radical, preventing the formation of dihydrobiphenyls, terphenyls, and quaterphenyls. The ability of oxygen to act in the same capacity has recently been demonstrated.

Heteroaromatic Compounds

The reactivities of carbon-hydrogen bonds *alpha* to several heterocyclic aromatic rings are listed in Table 16. These results indicate that the enhancement of reactivities toward phenyl radical abstractions at alkyl side chains provided by the aromatic rings follow the order: 2-, 3-, and 4-pyridyl $<$ 2-(5-)pyrazyl $<$ 2-furyl $<$ 3-thienyl

≤ N-pyrryl ≤ phenyl ≤ 2-thienyl ≤ 2-(5-)pyrryl. Whether or not this sequence reflects the abilities of aromatic groups to stabilize benzylic-type radicals is discussed below.

The difference between the reactivities of 2- and 3-methylthiophene was somewhat surprising. In order to confirm the higher reactivity of 2-thienyl derivatives, the relative reactivity of di-2-thienylmethane was determined. This compound was 3.1 times as reactive as diphenylmethane. The value for the reactivity of N-methylpyrrole is approximate. Pyrrole and N-methylpyrrole were studied in order to determine whether the nitrogen-hydrogen bond of pyrrole would contribute to the reactivity of its derivatives. This bond was found to be completely unreactive, but the amount of benzene formed in the competetive reactions between pyrrole and carbon tetrachloride (Table 2) was 0.035 mole/mole PAT. The difference between this value and the benzene correction of -0.054 mole/mole PAT introduces a large error in the observed reactivity of N-methylpyrrole.

The only examples available in the literature for comparison with the present study are the relative reactivities of 3- and 4-picoline toward the t-butoxy radical at 110 °C. Johnston and Williams (53) found 3- and 4-picoline to be 44% and 33% as reactive as toluene, respectively. The precision obtained in the present work did not permit the detection of any difference between the reactivities of the

Table 16. Relative reactivities of α carbon-hydrogen bonds of heteroaromatic compounds toward the phenyl radical at 60 °C

Compound	k_H/k_{Cl}[a]	Δ(DE)[b]	RE[c]
3-Picoline	0.15	2.438	23
4-Picoline	0.15	2.430	23
5-Collidine	0.17	2.440	23
2,5-Dimethylpyrazine	0.21	-0.463	--
2-Methylfuran	0.31	5.278	22
3-Methylthiophene	0.32	1.430	28
N-Methylpyrrole	0.3 - 0.4	-----	25
Toluene	0.36	2.430	36
2-Methylthiophene	0.58	2.365	28
2,5-Dimethyl pyrrole	0.95	2.276	25
Diphenylmethane	2.72	2.003	--
Di-2-thienylmethane	8.36	1.911	--

[a] Reactivity relative to single carbon-chlorine bond in carbon tetrachloride.

[b] Difference in delocalization energies between hydrocarbon and radical: $(DE)ArCH_3$ - $(DE)ArCh_2\cdot$; in units of β_0. Reference 54, p. 135.

[c] Resonance energy of unsubstituted aromatic ring from hydrogenation data. Reference 55, p. 98.

picolines. The picolines were found to be 42% as reactive as toluene toward the phenyl radical, in good agreement with the results of Johnston and Williams.

The differences in delocalization energies, Δ(DE), between the aromatic compounds and the corresponding benzylic-type radicals were calculated by Mr. E. T. Strom of these laboratories, using the simple Hückel molecular orbital treatment. The parameters and definitions of terms may be found in the book by Streitweiser (54). Values of α and β for heteroaromatics were expressed in terms of α_o and β_o (for benzene) by the equations

$$\alpha = \alpha_o + h\beta_o \quad , \tag{27}$$

and

$$\beta = k\beta_o \quad . \tag{28}$$

The following values of h and k were used: for pyridine derivatives, $h_N = 0.5$, $k_{CN} = 1.0$; for pyrrole derivatives, $h_N = 1.5$, $k_{CN} = 0.8$; for furan derivatives, $h_O = 2.0$, $k_{CO} = 0.8$. The sulfur atom in thiophene was treated as a modified vinyl group. This resulted in a benzene-type problem with $k_{12} = k_{56} = 0.8$, and all other k's and h's were assigned values of unity and zero respectively. The methyl groups in all compounds were treated as heteroatoms with $h_M = 2.0$ and $k = 0.7$. In no case was an auxiliary inductive parameter used.

As seen in Table 16, no simple relationship exists between the relative reactivity of a methyl-substituted heteroaromatic compound and the resonance energy (55) of the parent heterocycle, and no trend is apparent which is consistent with the difference in calculated delocalization energies (54) of the compound and its radical. Two possibilities are suggested here. First, the molecular orbital approach to the calculations may be too approximate to be of value in the present study. If this is the case, self-consistent field calculations could be of value. The second possibility for the lack of correlation is that the reactivities of these compounds are not governed by the relative stabilities of the product radicals. The writer is inclined to favor the first suggestion.

Compounds Containing Functional Groups

The effects of various functional groups on the reactivities of α-carbon-hydrogen bonds toward phenyl radicals are summarized in Table 17. The compounds are listed in order of decreasing enhancement by the respective functional groups, with the exception of the chloromethanes which are unique in this series. The reactivities of all carbon-hydrogen bonds were taken into account in the calculation of the relative

Table 17. Effects of functional groups on reactivities of carbon-hydrogen bonds toward the phenyl radical at 60 °C

Compound	k_H/k_{Cl}, α C-H bond			Enhancement		
	Prim.	Sec.	Tert.	Prim.	Sec.	Tert.
Trichloromethane			13			7.3
Dichloromethane		0.94			2.6	
Chloromethane	0.087			1.9		
Trimethylamine	1.44			32		
N,N-Dimethylaniline	1.9			42		
Thioanisole	0.49			11		
Methanol	0.18			4.0		
Dimethyl ether	0.18			4.0		
Anisole	0.12			2.7		
Acetone	0.12			2.7		
3-Pentanone		1.24			3.4	
Diisopropylketone			1.99			1.12
Acetic acid	0.11			2.4		
Methyl acetate	0.11			2.4		
Methyl benzoate	0.01			---		
Dimethyl malonate		0.36[a]			1.00	
2,4-Pentanedione		0.58[b]			1.62	
Acetonitrile	0.12			2.7		
Propionitrile		0.69			1.92	
Isobutyronitrile			2.69			1.51

[a] $k_H/k_{Cl} = \frac{4}{2}(0.180) - \frac{6}{2}(0.00)$.

[b] $k_H/k_{Cl} = \frac{4}{2}(0.471) - \frac{6}{2}(0.12)$.

Table 17. (Continued)

Compound	k_H/k_{Cl}, α C-H bond			Enhancement		
	Prim.	Sec.	Tert.	Prim.	Sec.	Tert.
Tetramethylsilane	0.094			2.1		
Phenyltrimethylsilane	0.089			2.0		
Neopentane	0.045			1		
Hexane		0.36			1	
3-Methylhexane			1.78			1
Nitromethane	0.06			1.33		
Nitroethane		0.30			0.83	
2-Nitropropane			0.70			0.40
Dimethyl sulfoxide	0.026			0.58		

reactivities of the α-carbon-hydrogen bonds. All carbon-hydrogen bonds in the *beta* position or more remote positions were assigned the values obtained from model alkanes (i.e.; primary, 0.038; secondary, 0.36; and tertiary, 1.78). These same values were used for calculating enhancements of secondary and tertiary α-carbon-hydrogen bonds. (Enhancement was defined earlier as the reactivity of a carbon-hydrogen bond divided by the reactivity of the paraffinic analogue.) Because most primary carbon-hydrogen bonds were members of isolated methyl groups (not attached to a long carbon chain), enhancements of primary α-carbon-hydrogen bonds were calculated on the basis of 0.045 for k_H/k_{Cl} of neopentane.

Reaction product studies of previous workers (47) have been relied upon somewhat in assigning reactivities, but enough model compounds have been included in the present study that conclusions regarding the predominant site(s) of attack by phenyl radicals are largely independent of other workers. This can be illustrated by considering the reactivities of methyl acetate, methyl benzoate, and acetic acid, which have total reactivities of 0.084, 0.01, and 0.084 respectively. The values lead to the conclusions that the methyl group attached to the oxygen in methyl acetate has a reactivity of zero, and that hydrogen abstraction takes place at the acetyle carbon-hydrogen bonds with the same velocity in the cases of acetic acid and methyl acetate. These conclusions are supported by the observations of previous workers. Kharasch and Gladstone (56) have reported the formation of succinic acid arising by dimerization of the radicals produced by the attack of methyl radicals on acetic acid. Wijnen (57) determined the energy of activation for hydrogen abstraction by the methyl radical for methyl acetate in the gas phase. He commented that the energies of activation for abstraction reactions with acetic acid (58), methyl acetate (57), and acetone (59) were the same within experimental error. The formation of methyl propionate in the gas phase photolysis (57) of methyl acetate indicates the main path of the abstraction reaction:

$$\cdot CH_3 + CH_3CO_2CH_3 \longrightarrow CH_4 + \cdot CH_2CO_2CH_3 \qquad (29)$$

$$\cdot CH_3 + \cdot CH_2CO_2CH_3 \longrightarrow CH_3CH_2CO_2CH_3 \quad . \qquad (30)$$

A comparison of transfer reactions of the methyl and phenyl radicals (Figure 6) reveals general agreement between the two sets of data as to the effect of functional groups upon reactivity.

The enhancement of reactivities of carbon-hydrogen bonds in a position alpha to many functional groups has been known for some time from studies involving free radical addition of various functionally substituted compounds to olefins (47). A significant conclusion to be drawn from the present work is that the enhancement due to functional substitution is not as great as is generally supposed. With the exceptions of amines and sulfides, most carbon-hydrogen bonds alpha to functional groups are less than four times as reactive as their paraffinic counterparts.

Examination of Table 17 shows that the effect of disubstitution is not additive. A secondary carbon-hydrogen bond adjacent to a carbonyl group (3-pentanone) exhibits an enhancement of 3.4, while the methylenic α-carbon-hydrogen bonds in dimethyl malonate and 2,4-pentanedione show enhancements of 1.00 and 1.62 respectively. The chloromethanes are exceptional in this respect, the reactivity increasing approximately ten-fold with each additional chlorine atom in the molecule. As shown in Table 3, no chlorine abstraction by the phenyl radical occurs with the chloromethanes. The abstraction reactions of methyl radicals (Figure 6) with methyl chloride, methylene chloride, and chloroform are in general agreement with the results of the present study. However the enhancement due to the proximity of chlorine seems to be greater in reactions of the methyl radical.

The enhancement of reactivity supplied by a functional group seems to decrease with increasing alkyl substitution at the *alpha* carbon. This phenomenon is well defined in the reactivities of the nitrile series, where the enhancement decreases from 2.7 to 1.92 to 1.51 for primary, secondary, and tertiary α-carbon-hydrogen bonds respectively. The decrease in enhancement observed in the nitroalkane series is more severe, going from 1.33 for the primary to 0.40 for the tertiary α-carbon-hydrogen bond. The ketones are not so well defined; the enhancement observed in 3-pentanone is slightly greater than that of acetone. Diisopropyl ketone is of special interest because of its steric similarity to 2,4-dimethylpentane. The low reactivities of the tertiary α-carbon-hydrogen bonds observed for this ketone are consistent with the explanation offered earlier for the low reactivity of

2,4-dimethylpentane. Using "normal" values of 0.038 and 0.36 for the respective reactivities of primary and secondary carbon-hydrogen bonds in 2,4-dimethylpentane results in a calculated value of 0.73 for the reactivity of each tertiary carbon-hydrogen bond in this compound. On this basis the enhancement offered by the carbonyl group in diisopropyl ketone is calculated to be 2.7, about the same as that observed for acetone.

The steric factors discussed above seem to be general for free radical reactions involving compounds with functional groups. Data for reactions of the methyl radical (24) show that enhancements in the reactivities of ethers decrease with increasing substitution from 5 in dimethyl ether to 1.27 in diisopropyl ether. The enhancements observed in alcohols decrease in the order 6.7, 4.8, and 2.1 for primary, secondary, and tertiary carbon-hydrogen bonds respectively.

The very low reactivity of dimethyl sulfoxide is consistent with its low radical stabilization factor ($Q = 0.1$) as determined from copolymerization experiments by Price and Zomlefer (60). Price and Gilbert (61) found the radical stabilization factor for methyl vinyl sulfone to be 0.07 to 0.15. The relative reactivity of dimethyl sulfone toward the phenyl radical could not be determined because of its insolubility in carbon tetrachloride.

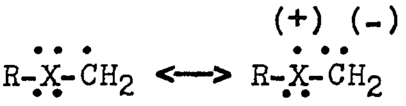
The possibility of secondary reactions should be mentioned here. Grieve and Hey (10) found that decomposition of nitrosoacetanilide in methanol produced some formaldehyde, presumably by the path

$$Ph\cdot + CH_3OH \longrightarrow PhH + \cdot CH_2OH \qquad (31)$$

$$R\cdot + \cdot CH_2OH \longrightarrow CH_2O + RH \quad . \qquad (32)$$

If R = Ph, the secondary reaction would tend to make the observed reactivity too high. Secondary reactions are believed to be unimportant in the present study because of the high concentration of trityl radicals present during all reactions. (See Results section.)

The degrees of enhancement provided by heteroatoms adjacent to carbon-hydrogen bonds were observed to be nitrogen > sulfur > oxygen. This is approximately the reverse order of the electronegativities of the elements, indicating that the contribution of resonance form II is less in the case of oxygen due to its higher electronegativity. Since sulfur and carbon



$$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}-\dot{C}H_2 \longleftrightarrow R-\overset{(+)}{\overset{\cdot}{\underset{\cdot\cdot}{X}}}\overset{\cdot\cdot}{-}\overset{(-)}{C}H_2 \qquad (33)$$

I II

are of the same electronegativity it follows that radical anions of carbon compounds should gain substantial stability from resonance of the same type. The stability

$$R_2\overset{(-)}{\overset{\circ\bullet}{C}}-\overset{\bullet}{C}R_2 \longleftrightarrow R_2\overset{\bullet}{C}-\overset{(-)}{\overset{\bullet\bullet}{C}}R_2 \qquad (34)$$

of radical anions of carbon compounds has been confirmed in these laboratories by Messrs. E. T. Strom and E. G. Janzen who have also prepared radical anions of azo compounds.

Compounds Containing Hydrogen and Chlorine Bonded to Elements Other than Carbon

The relative reactivities of several compounds containing hydrogen atoms bonded to heteroatoms are listed in Table 18. In the compounds investigated the silicon-hydrogen bonds were more reactive toward transfer reactions by the phenyl radical than were the analogous carbon-hydrogen bonds. This is consistent with the observations of Curtice, Gilman, and Hammond (62) who found the chain transfer constant (styrene polymerization) of triphenylsilane to be greater than that of the carbon analogue.

The relative reactivity assigned to diphenylphosphine is a questionable estimate of order of magnitude. The reactions of alkyl- and aryl-substituted phosphines with carbon tetrachloride were recently rediscovered (63-65). As described in the experimental section, the reaction of diphenylphosphine with carbon tetrachloride takes place to a substantial degree at 60°. This decreases the concentration of phosphine and

Table 18. Relative reactivities toward the phenyl radical of hydrogen atoms bonded to several elements

Compound	Bond reacting	k_H/k_{Cl} 60°
Triphenylsilane	Si-H	19.0
Triphenylmethane	C -H	13.9
Diphenylsilane	Si-H	15.4
Diphenylmethane	C -H	2.72
Diphenylamine	N -H	9.0
Diphenylphosphine	P -H	> 400 (?)

causes the observed reactivity to be too low. The matter is further complicated by the probability that phenyl radicals add to trivalent phosphorus quite readily (see below). The numerical value for the reactivity of diphenylphosphine listed in Table 18 is not considered significant, but its order of magnitude is consistent with the observation of Pellon (66) that the addition of phosphinyl radicals to olefins is a reversible process. The relative reactivities of triphenylmethane and diphenylamine do not differ greatly; the radicals derived from both these compounds possess a considerable degree of stability. Because of the complications of side reactions between diphenylphosphine and carbon tetrachloride, the suggestion is quite tentative that the reactivity toward phenyl radicals of a phosphorus-hydrogen bond is greater than that of a nitrogen-hydrogen bond.

While the study of reactions of phenyl radicals with phosphorus trichloride and silicon tetrachloride is incomplete at present, these compounds will be discussed briefly. As shown in Table 4, no abstraction products were obtained when either phenylazotriphenylmethane or benzoyl peroxide was decomposed in phosphorus trichloride or mixtures of phosphorus trichloride with cyclohexane. The ability of phosphorus trichloride to protect cyclohexane from abstraction by phenyl radicals must be attributed to an exceptionally fast addition reaction involving phenyl radicals and phosphorus trichloride. While the data at hand do not allow a detailed interpretation, it is likely that the fate of the phenyl radicals can be explained by the reaction proposed by Mayo (67):

$$R\cdot + PCl_3 \rightleftarrows \dot{R}PCl_3 \quad , \qquad (35)$$

where R = cyclohexyl. Mayo has suggested that Reaction 35 is extremely fast and reversible, and observed that phosphorus trichloride competes well with oxygen for cyclohexyl radicals. The speed of Reaction 35 becomes apparent only when it is rendered irreversible by a fast reaction of the radical $\dot{R}PCl_3$ with some reactive intermediate, according to Mayo. In Mayo's system the $\dot{R}PCl_3$ radical reacts with oxygen or p-xylylene. In the present study this radical could react with triphenylmethyl or some other radical. It is significant that the chlorination of cyclohexane was not observed in reactions of phenyl radicals with mixtures of cyclohexane and phosphorus trichloride. The suggestion (67) that Reaction 35 may apply generally to free radical reactions of trivalent phosphorus is supported by the very low yield of abstraction products obtained from the decomposition of PAT in a carbon tetrachloride solution of triphenylphosphine (Table 2).

The reactions of phenyl radicals with silicon tetrachloride yield benzene as the major product. This phenomenon is not understood. Examination of Table 4 reveals that benzene is produced in about 64 to 75% yield when either PAT or benzoyl peroxide is decomposed in silicon tetrachloride. It seems unlikely that the phenyl radicals are abstracting hydrogen atoms from the other 25 to 35% of organic material in the reaction mixtures. It is believed that some labile intermediate is formed which is hydrolyzed at some time during the experimental procedure to give benzene. It was confirmed (see Experimental) that phenyltrichlorosilane did not hydrolyze to give benzene during the basic hydrolysis which was preliminary to GPC analysis.

Reactions of Phenyl Radicals with Oxygen

The influence of oxygen upon the yields of abstraction products of phenyl radicals affords a method of estimating the relative reactivity of oxygen toward phenyl radicals. The following reactions are assumed:

$$CCl_4 + Ph\cdot \xrightarrow{4k_{Cl}} Cl_3C\cdot + PhCl \tag{36}$$

$$O_2 + Ph\cdot \xrightarrow{k_{O_2}} PhO_2\cdot \tag{37}$$

$$PhO_2\cdot \longrightarrow Products \quad . \tag{38}$$

Further assumptions are the same as discussed earlier in connection with the addition of phenyl radicals with the alkenes. The kinetic expressions reduce to

$$\frac{k_{O_2}}{4k_{Cl}} = \frac{(CCl_4)((PhCl)_i - (PhCl)_p)}{(O_2)(PhCl)_p} \quad , \tag{39}$$

where $(PhCl)_i$ = yield of chlorobenzene in the absence of oxygen,

and $(PhCl)_p$ = yield of chlorobenzene in the presence of oxygen.

Numerical values of these quantities appear in Tables 5 and 6 for the competetive reactions of oxygen with carbon tetrachloride and cyclohexane, respectively.

The solubility of oxygen at 60 °C was taken as 0.016 M (0.0025 mole fraction), the value reported for isooctane (68) at one atmosphere. Henry's Law was used to calculate solubilities at other pressures. The applicability of Henry's Law to carbon tetrachloride (69) and hydrocarbons (70) has been well demonstrated, and the assumption that the solubility of oxygen is the same in most hydrocarbons is accurate within 20 per cent relative error (71).

From the competitive reactions of oxygen with carbon tetrachloride (Table 5) and cyclohexane (Table 6) the quantities k_{O_2}/k_{Cl} and k_{O_2}/k_H were determined to be 3×10^3 and 10^4 respectively. The quotient of these values results in k_H/k_{Cl} of 0.3, in fair agreement with the value of 0.36 determined directly by the competitive reactions between carbon tetrachloride and cyclohexane. These experiments show that oxygen adds to phenyl radicals 10^3 - 10^4 times more rapidly than abstraction reactions take place. It has been determined that addition of oxygen to alkyl radicals occurs 10^6 - 10^8 times as rapidly as peroxy radical attack on carbon-hydrogen bonds (47). If abstraction reactions of phenyl radicals and peroxy radicals proceed at comparable rates, the reaction rate of phenyl radicals with oxygen is 10^{-3} to 10^{-4} that of the rate of reaction of a typical alkyl or allyl radical with oxygen. Hammond and Nandi (72) have suggested that phenyl radicals may be incapable of reaction with oxygen in order to account for the anomalous behavior of benzoyl peroxide as an oxidation initiator in some systems. While the present results show that phenyl radicals do react with oxygen, the rate may be slow enough to support this speculation.

Neither diphenyl peroxide nor the corresponding hydroperoxide has been reported in the literature, and evidence for Reaction 37 has been indirect in most cases. The phenylperoxy radical is generally assumed to give phenolic products. Reaction 37 has been postulated to account for the influence of oxygen upon the reaction of benzene with Fenton's Reagent (73), the slow rate of oxidation in acid media of alkylbenzoic acids (74), the effect of oxygen upon the radiolysis (75) of benzene, and the vapor phase oxidation (76) of benzene. Small amounts of oxygen have no effect on the partial rate factors observed in homolytic arylation (77) and slightly enhance the yields of biaryls.

Isotope Effects and Thermodynamic Considerations

The intermolecular deuterium isotope effect (78) for abstraction reactions of phenyl radicals was determined for two compounds; k_D/k_H at 60 $^\circ$C was found to be 0.22 ± 0.035 for toluene and $0.227\,^{+0.004}_{-0.02}$ for acetone. Each value has been corrected for isotopic purity of the deuterium compound (see Experimental), which was accurately known for toluene-α-d_3 (99.5%) and was estimated to be 97 - 100% for acetone-d_6.

Melander (79) has calculated by approximate equations the isotope effects expected at various temperatures for cleavage of the carbon-hydrogen bond. If only the zero-point energy of the stretching vibration is assumed to be lost on passing into the transition state, a value of k_D/k_H of 0.15 is expected at 60 °C. If all three hydrogen vibrations are lost in the transition state a value of 0.09 is predicted for k_D/k_H at 60 °C.

While the value of k_D/k_H determined in the present work does not reveal a maximum isotope effect in transfer reactions of the phenyl radical, it does indicate appreciable bond-breaking in the transition state. As shown in Table 19, the deuterium isotope effect is somewhat lower in transfer reactions of the phenyl radical than the values reported by various workers for the methyl radical. This is consistent with the slightly lower degree of the selectivity of the phenyl radical.

The relationship between bond dissociation energy and relative reactivity toward the phenyl radical is shown in Figure 5. With the exception of cyclohexane, all bond dissociation energies have been taken from the book by Cottrell (35). The value used for cyclohexane, 91 kcal/mole, was that of Pottie, Harrison, and Lossing (80).

By assuming constant A factors and applying Polanyi's Rule (Equation 20), it is possible to establish an approximate

Table 19. Isotope effects for abstraction reactions of various radicals

Radical	Substrate	k_H/k_D	
Chlorine	Toluene	2.0	(80°)[a]
t-Butoxy	Ethylbenzene	3.7	(107 - 116°)[a]
Bromine	Toluene	4.8	(77°)[a]
Peroxy	Cumene	5.5	(60°)[a]
Methyl-d_3	Methanol	7.1	(30°)[b]
Methyl	Ethylbenzene	10	(60°)[c]
Methyl	Toluene	$\leq$ 7	(125°)[d]
Phenyl	Toluene	3.1 - 5.5	(110 - 116°)[d]
Phenyl	Toluene	4.6	(60°)[e]
Phenyl	Acetone	4.4	(60°)[e]

[a] Reference 26.

[b] Reference 81.

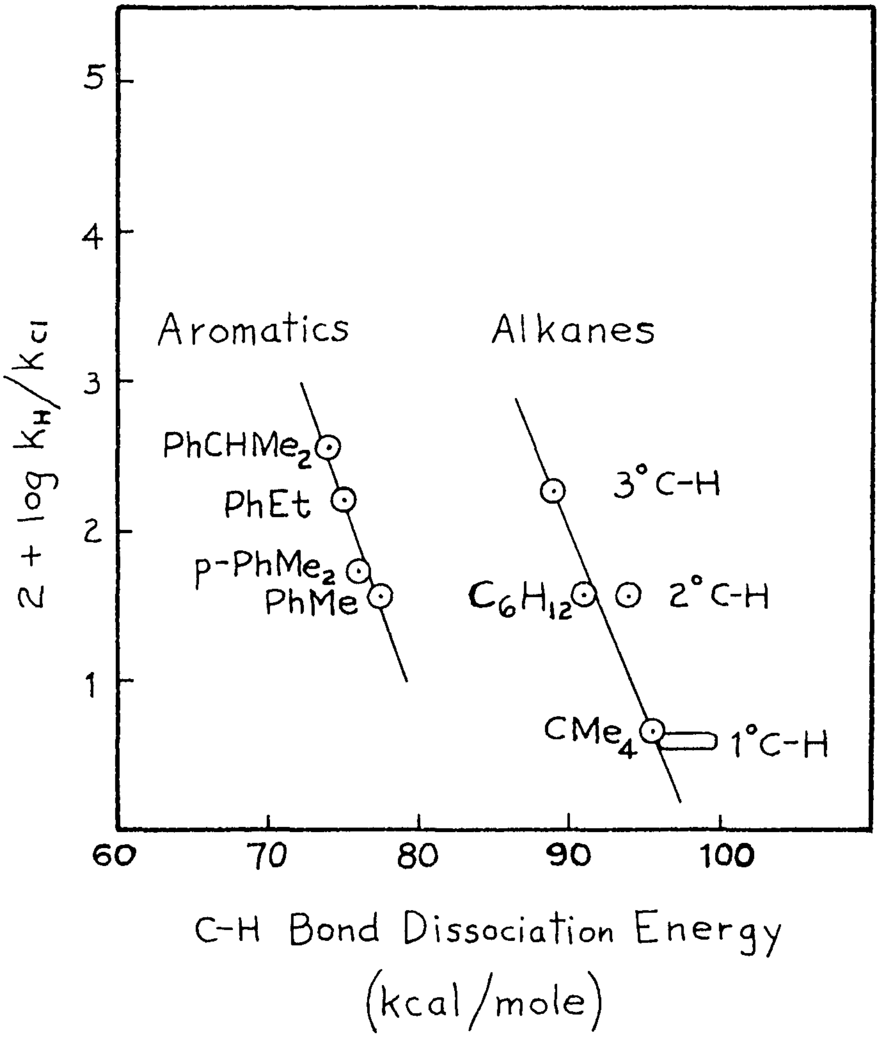
[c] Reference 82, calculated from $E_a^D - E_a^H = 1.56$ kcal/mole, assuming ratio of A factors to be unity.

[d] Reference 83.

[e] Present work.

relationship between heats of reaction and the relative reactivities of various carbon-hydrogen bonds toward abstraction reactions of the phenyl radical. The Arrhenius equation (24) may be written in the integrated form

Figure 5. Relationship between reactivities of several hydrocarbons toward phenyl radicals and bond dissociation energies



Aromatics
Alkanes
PhCHMe$_2$
PhEt
p-PhMe$_2$
PhMe
3° C-H
C_6H_{12}
2° C-H
CMe$_4$
1° C-H
5
4
3
2
1
60
70
80
90
100
2 + log k_H/k_{Cl}
C-H Bond Dissociation Energy
(kcal/mole)

$$k = A \exp(-E_a/RT) \quad , \tag{40}$$

which is reduced to

$$2.3\ RT \log k = 2.3\ RT \log A - E_a \quad . \tag{41}$$

If A is assumed to be constant,

$$2.3\ RT\ \Delta \log k = -\Delta E_a \quad . \tag{42}$$

From Polanyi's rule (Equation 20)

$$\alpha = -\frac{\Delta E}{\Delta(\Delta H)} = \frac{2.3\ RT\ \Delta \log k}{\Delta H} \quad . \tag{43}$$

At 60 $^{\circ}$C,

$$\alpha = (1{,}520)\,\frac{\Delta \log k}{\Delta H} \quad . \tag{44}$$

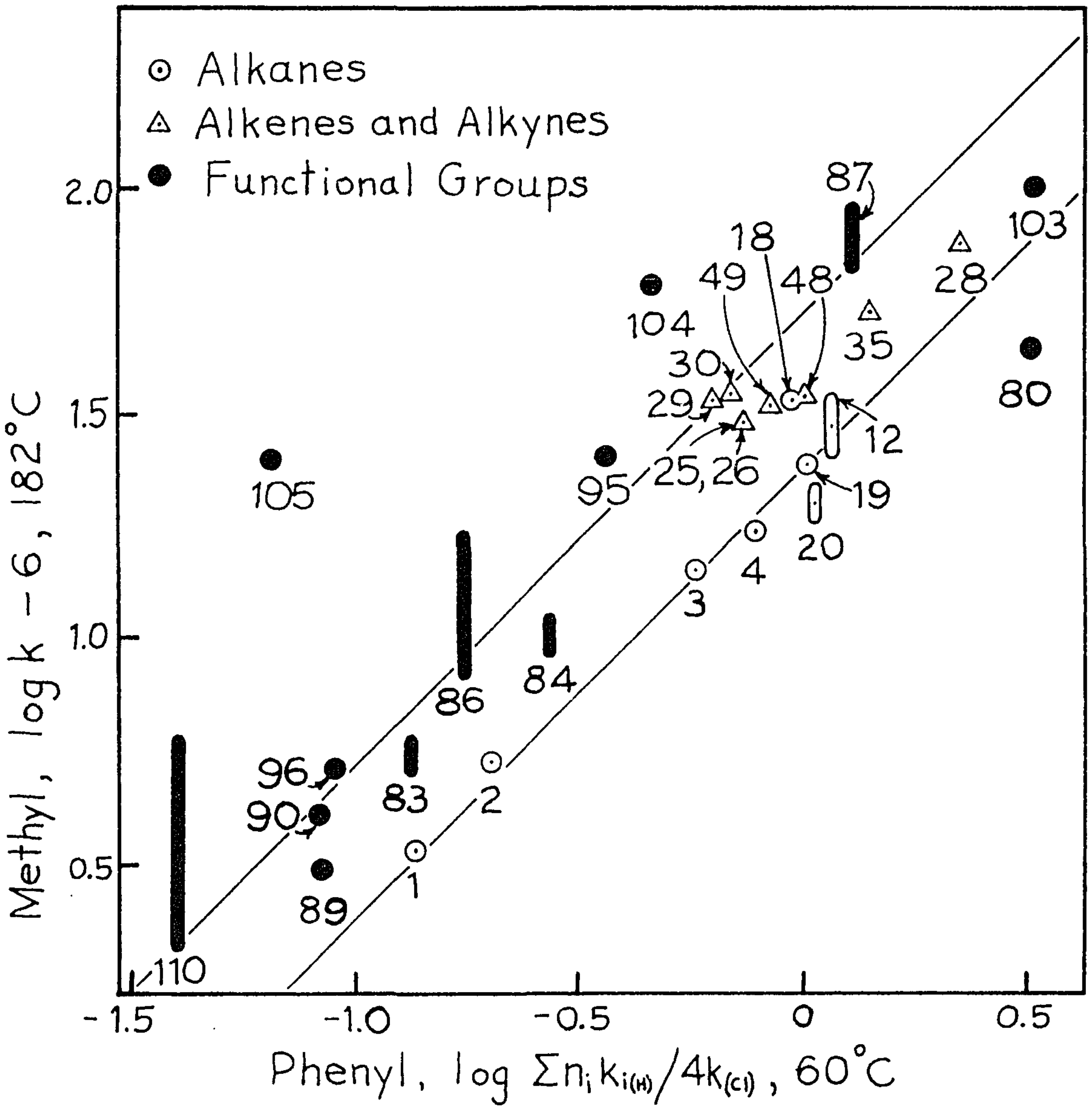
In Figure 5 the data for alkanes and aromatic hydrocarbons fall on two different lines which are approximately parallel. This is probably due to a significant difference in A factors between the two series, as they would be expected to lie on the same line if the ordinate were energies of activation. Brook (39) found that the energies of activation involves in abstraction reactions of the t-butoxy radical were about 4 kcal/mole greater for the alkanes than for aralkyl hydrocarbons, and commented on the unfavorable entropy effect in the aromatic series. Meyer, Stannett, and

Szwarc (51) have recently discussed conformational analysis of radical abstractions at side-chains of alkyl benzenes.

The value of α calculated from the slopes of the lines in Figure 5 is 0.4. Trotman-Dickenson (84) has reported α to be 0.5 for abstraction reactions of the methyl radical.

A comparison is made in Figure 6 of the logarithms of reactivities of 28 compounds toward abstraction reactions by the methyl and phenyl radicals. Most of the points lie within a band of slope unity, indicating equal increments of energies of activation for the two radicals. (Such a comparison neglects A factors.) The agreement among the paraffins and cyclic paraffins is particularly good. The olefins appear to cluster about a single point. Trotman-Dickenson (24) has mentioned that the olefins are unique in the respect that their reactivities are governed by A factors, the activation energies of all olefin transfer reactions yet measured being the same within experimental error. The chloromethanes provide the largest deviation from the "line" of any class of compounds (Reactions 105, 104, 103). The reactivities of these compounds form a line of their own and the chloromethanes seem to be considerably more reactive toward methyl than toward phenyl radicals.

Figure 6. Comparison of the selectivities of methyl and phenyl radicals involved in abstraction reactions


⊙ Alkanes
△ Alkenes and Alkynes
● Functional Groups
Methyl, log k − 6, 182°C
Phenyl, log $\Sigma n_i k_{i(H)}/4k_{(Cl)}$, 60°C
2.0
1.5
1.0
0.5
-1.5
-1.0
-0.5
0
0.5
1
2
3
4
12
18
19
20
25,26
28
29
30
35
48
49
80
83
84
86
87
89
90
95
96
103
104
105
110

EXPERIMENTAL

Melting points and boiling points are uncorrected. Compounds studied in this work are grouped rather arbitrarily according to functional groups and reactivities. The numbered order appearing in Table 2 is followed approximately throughout this thesis.

Chemicals

Distillation was relied upon heavily for the purification of liquids. Fractionations at atmospheric pressure were carried out in a Todd Distillation Apparatus. A Vigreaux column of about four inches length was used for most vacuum distillations. When better separation was required of distillations at reduced pressure, a 16 inch spinning band column was used.

Carbon tetrachloride was Mallinckrodt Reagent Grade and was passed through silica gel before use. Examination by gas phase chromatography (GPC) showed less than 0.1 mole per cent impurities.

Alkanes were examined by GPC and ultraviolet absorption for the presence of impurities, especially benzene and toluene. When necessary, alkanes were treated with fuming sulfuric acid, washed, dried, and fractionated. All alkanes used in this study were nearly transparent in the ultraviolet region and were definitely free of aromatic compounds. In the following descriptions per cent purity refers to mole per cent unless otherwise specified.

Dimethylpropane (Phillips Petroleum Company) had a minimum purity of 99.92%.

Tetramethylbutane (Aldrich Chemical Company) was *purissimum* grade. No impurities were detected by GPC.

Pentane (Matheson, Coleman, and Bell) was fractionated. The fraction used had a purity of 99.9% by GPC.

Hexane (Phillips Petroleum Company) was treated with fuming sulfuric acid and fractionated. Minimum purity was 99% by GPC.

Heptane (Matheson, Coleman, and Bell) was fractionated to a minimum purity of 99%.

Octane (Phillips Petroleum Company) was used without further purification. It was *pure* grade (minimum purity 99%).

Hexadecane (Humphrey-Wilkinson, Inc.) had a minimum purity of 99%.

3-Methylpentane (Phillips Pure Grade) was used without further purification.

2-Methylpentane (Phillips Research Grade) was fractionated before use. Minimum purity was 99.9%.

2,2-Dimethylbutane (Phillips Pure Grade) was used as received.

3-Methylhexane (Phillips Petroleum Company) was technical grade (95% minimum purity). Its gas phase chromatogram showed less than one per cent of impurities and it was used without further purification.

2,3-Dimethylbutane, 2,4-dimethylpentane, 2,2,4-trimethylpentane, 2,2,5-trimethylhexane, and 2,3,4-trimethylpentane were obtained from the Phillips Petroleum Company. Each had a minimum purity of 99% and was used as received.

2,2,3-Trimethylbutane was a gift of Socony Mobile Oil Company. Its purity was greater than 99 mole per cent and it was used as received.

2,5-Dimethylhexane was purchased from the California Corporation for Biochemical Research and had a minimum purity of 98%.

Cyclopentane (Phillips Pure Grade) was treated with fuming sulfuric acid and fractionated. Its purity was estimated to be 99.5% by GPC.

Cyclohexane from Eastman Kodak Company was spectro grade and contained less than one mole per cent impurities.

Cycloheptane (Madison Laboratories) was fractionated by previous workers (29) and showed a minimum purity of 99.9% by GPC.

Cyclooctane was a gift of Cities Service Research and Development Company. After acid treatment and distillation, a middle fraction showed no impurities by GPC.

Methylcyclopentane and methylcyclohexane (Phillips Petroleum Company) were subjected to acid treatment and fractionation. Each had a minimum purity of 99%.

cis-2-Butene and *trans*-2-butene (The Matheson Company) were C. P. grade, 99% minimum purity.

2-Methyl-2-butene, a gift of Enjay Chemical Company, had a purity of 98% by volume and was used without further treatment.

2,3-Dimethyl-2-butene was prepared and purified by the procedure of Kistiakowsky (85) and showed a minimum purity of 99.5% by GPC. It was passed through silica gel immediately before use.

1-Butene, 2-pentene (*cis*-*trans* mixture), 2-methyl-1-butene, 3-methyl-1-butene, and propylene were from Phillips Petroleum Company. Each had a minimum purity of 99% and was used without further purification.

1-Pentene (Phillips Petroleum Company) had a minimum purity of 95% and was used as received.

4-Methyl-2-pentene (Phillips 99%) was fractionated before use.

1-Octene (Matheson, Coleman, and Bell) was fractionated. A middle fraction was of 99% minimum purity by GPC.

2-Octene (*cis*-*trans* mixture) from the Aldrich Chemical Company was fractionated. The portion used was greater than 99% pure by GPC.

2,3,3-Trimethyl-1-butene of 98% purity was obtained from the Petroleum Refining Laboratory, Pennsylvania State University. It was fractionated before use.

3,3-Dimethyl-1-butene (K and K Laboratories) was >99% pure by GPC and was used as received.

1,3-Pentadiene (cis-trans mixture) was a gift of Enjay Chemical Company. After fractionation it was 95 - 97% pure.

2-Phenylpropene (Eastman Kodak Company) and 1-phenylpropene (K and K Laboratories, Inc.) were >99% pure by GPC after distillation.

Cyclopentene and cyclohexene were Phillips Research Grade. No purification was necessary.

3-Phenylpropene (Matheson, Coleman, and Bell) showed a purity of 98 - 99% by GPC after fractionation.

2,5-Dimethyl-2,4-hexadiene, a sample from Eastman Kodak Company, was fractionated under high reflux. A small center fraction was found to be >99% pure by GPC.

Propyne (The Matheson Company) was of 95% minimum purity.

1-Butyne (National Bureau of Standards) contained impurities to the extent of 0.13 ± 0.07 per cent.

2-Butyne (National Bureau of Standards) contained impurities to the extent of 0.069 ± 0.038 per cent.

t-Butylbenzene (Phillips 99%) was passed through silica gel before use.

Toluene (Fisher Reagent Grade) was fractionated. Minimum purity was 99.9% by GPC.

p-Chlorotoluene (Matheson, Coleman, and Bell) contained about 0.8% of the meta isomer by GPC.

m-Chlorotoluene (Matheson, Coleman, and Bell) was fractionated to remove traces of toluene. The fraction used was >99% pure.

p-Phenoxytoluene was prepared by Mr. R. C. Williamson of these laboratories by allowing p-methylphenoxide to react with bromobenzene in the presence of a catalytic quantity of copper at 270 °C. The reaction mixture was washed, dried, and distilled, b. p. 110 - 111°/2 mm. The absence of the meta isomer, bromobenzene, and volatile impurities, was ascertained by gas chromatography. The liquid was passed through silica gel before use.

p-Nitrotoluene (Eastman Kodak Company) was recrystallized from ethanol, m. p. 50.5 - 51 °C. No volatile impurities or recrystallization solvent appeared on a gas chromatogram of this material.

p-Xylene (Phillips Research Grade) showed no impurities by GPC.

Mesitylene (National Bureau of Standards) contained 0.05 ± 0.02 mole per cent impurities.

Ethylbenzene (Matheson, Coleman, and Bell) was fractionated and dried over anhydrous sodium sulfate. The fraction used displayed no peaks in the gas chromatogram due to impurities.

Cumene (Phillips 99%) was used as received.

Diphenylmethane (Eastman Kodak Company) was fractionated and had a minimum purity of 99%.

Triphenylmethane (Matheson, Coleman, and Bell) was recrystallized from an ethanol-benzene mixture, m. p. 93.5 - 94 °C. The gas chromatogram of a carbon tetrachloride solution of the recrystallized material indicated the absence of volatile impurities.

Indan and tetralin (Aldrich Chemical Company) were fractionated and each was >99% pure.

Hexamethylbenzene (Eastman Kodak Company), m. p. 164 - 165°, was used without further purification.

Biphenyl (Matheson, Coleman, and Bell), m. p. 68 - 70°, was used as received.

Triphenylamine (Eastman Kodak Company), m. p. 113 - 119°, was used as received.

Diphenyl ether (Eastman Kodak Company) was passed over silica gel before use. Analysis by GPC showed no volatile impurities.

Triphenylphosphine (Metal and Thermit Corp.) was recrystallized from ethanol, m. p. 80 - 81 °C.

3-Picoline (Matheson, Coleman, and Bell) was fractionated. The minimum purity of a center fraction was 95% by GPC.

4-Picoline (Matheson, Coleman, and Bell) showed a minimum purity of 98% by GPC after fractionation.

s-Collidine (Eastman Kodak Company) was dried over potassium hydroxide pellets and was 99% pure by GPC.

2,5-Dimethylpyrazine was a gift of the Wyandotte Chemicals Corporation. After fractionation to remove colored materials its purity was >99% by GPC.

2-Methylfuran (Matheson, Coleman, and Bell) had a purity of 99.5% by GPC after fractionation.

3-Methylthiophene (Aldrich Chemical Company) was 99.4% pure by GPC after two fractionations.

2-Methylthiophene was a gift of Socony Mobile Research Laboratories. The minimum purity by GPC was 95% after one fractionation. Because a limited quantity was available, a second fractionation was not feasible. A spot test with silver nitrate solution indicated the absence of mercaptan.

Di-2-thienylmethane was prepared by Mr. Joseph Schoeb of these laboratories according to a published procedure (86). After recrystallization from methanl its m. p. was 43 - 45 °C. Examination by GPC of a carbon tetrachloride solution showed that no methanol was retained by the crystals.

Pyrrole and N-methylpyrrole (Aldrich Chemical Company) were distilled just before using. The purity of each was somewhat better than 99% by GPC.

2,5-Dimethylpyrrole of unknown source was obtained from the collection of chemicals of these laboratories. Its identity was verified by physical properties (b. p. 78°/24 mm, d_4^{20} 0.937, n_D^{20} 1.5053), all of which compare well with literature values. The infrared spectrum was identical with the published spectrum (87). Its purity was >99% by GPC.

Trimethylamine (Eastman Kodak Company) was estimated to have a purity of 99% by GPC.

N,N-Dimethylaniline (Matheson, Coleman, and Bell) was distilled under vacuum, b. p. 41 - 43°/0.7 mm.

Thioanisole (Aldrich Chemical Company) was distilled under vacuum, b. p. 87 - 88°/21 mm. A middle fraction had a minimum purity of 98% by GPC.

Methanol (Baker Analyzed Reagent) was 99.8% pure.

Acetone (Baker Analyzed Reagent) was 99.5% pure.

Dimethyl ether (The Matheson Company) had a minimum purity of 99.5%.

Anisole (Eastman Kodak Company) showed a minimum purity of 99% by GPC.

3-Pentanone (Eastman Kodak Company) was fractionated. The center cut was >99% by GPC.

Diisopropyl ketone (Columbia Organic Chemicals Company) was fractionated until a fraction showing a minimum purity of 99% by GPC was obtained.

Acetic acid (Baker Analyzed Reagent) was used without further purification.

Methyl acetate was prepared by Mr. Paul Barks from acetic acid and methanol. The ester was found to be an azeotrope with methanol. Methanol was removed by passing the liquid through a 460 x 20 mm silica gel column and collecting only the first 40 ml eluted. This first fraction was free of methanol and was >99% pure after fractionation.

Methyl benzoate (Matheson, Coleman, and Bell) was used as received. Its gas chromatogram showed no volatile impurities.

Dimethyl malonate (Matheson, Coleman, and Bell) was distilled under vacuum. A middle fraction, b. p. $77^{\circ}/15$ mm, was used.

2,4-Pentanedione (Eastman Kodak Company) was fractionated. Minimum purity was 99% by GPC.

Isobutyronitrile and propionitrile (Eastman Kodak Company) each had a minimum purity of 99% by GPC after fractionation.

Acetonitrile (Matheson, Coleman, and Bell) was distilled twice over phosphorus pentoxide, once over potassium carbonate, then fractionated. Its purity was 99.9% by GPC.

Tetramethylsilane (Anderson Chemical Company) was

99.5% pure by GPC.

Phenyltrimethylsilane was a gift of General Electric Company Research Laboratories. After fractionation the purity was greater than 99%.

2-Nitropropane, nitroethane, and nitroethane (Eastman Kodak Company) were fractionated. Their minimum purities were 97%, 94%, and 99%, respectively, by GPC. The impurity in nitroethane was nitromethane.

Dimethyl sulfoxide (Crown Zellerbach) was distilled under vacuum before use. Its chromatogram showed no volatile impurities.

Chloroform and methylene chloride (Baker Analyzed Reagent) were fractionated before using and each had a minimum purity of 99.5%.

Methyl chloride (C. A. F. Kahlbaum Chemische Fabrik, GMBH; Schering-Kahlbaum A. G.) showed a purity of 98.5% by GPC.

Diphenylsilane (Andron Chemical Company) was distilled, b. p. 95 - 96°/2 mm, and was 97% pure by GPC.

Diphenylamine (Matheson, Coleman, Bell) melted at 55 - 56 $^{\circ}$C.

Diphenylphosphine was a gift of Mr. Gerald Schwebke, who prepared it by hydrolyzing lithium diphenylphosphorus with ice water (88). Analysis by GPC showed it to be 94% pure after distillation, b. p. 106 - 108°/2 mm, n_D^{20} 1.6242.

The infrared spectrum showed strong phosphorus-phenyl absorption at 6.95 microns and phosphorus-hydrogen adsorption at 4.35 microns.

Dimethylphenylphosphine was prepared after the procedure of Meisenheimer (89). It was distilled twice, b. p. 68 - 70°/9 mm and 45 - 46°/2 mm, to yield an oil which was 95 - 96% pure by GPC. The refractive index was n_D^{20} 1.5651. The boiling points agree well with the published vapor pressure data (90).

Trimethylchlorosilane (Anderson Chemical Company) had a minimum purity of 99% by GPC.

Silicon tetrachloride from Matheson, Coleman, and Bell was 99.8% pure.

Phosphorus trichloride was Merck Reagent Grade.

Acetone-d_6 was prepared by Mr. R. S. Nicholson according to the following procedure. Acetone (60 gm, Baker Analyzed Reagent, dried with calcium chloride) was equilibrated at room temperature for 36 hours with 50 gm deuterium oxide to which had been added potassium carbonate (200 mg). The acetone was then fractionally distilled through a 27 x 1.4 cm column packed with 1/4 inch glass helices. This procedure was repeated four more times to yield acetone-d_6 (ca. 60 ml, 79% yield) with a minimum isotopic purity of 97%. (The C-H frequency was absent in the infrared spectrum of the final product. The previous fraction contained about 6%

protium. Assuming that half of the remaining protium atoms were exchanged during the final treatment results in a value of about 3% H^1.)

Toluene-α-d_3 was prepared after the procedure of Renaud and Leitch (91). High resolution NMR analysis by Dr. R. W. King yielded a value for the isotopic purity of 95.0 ± 0.1%, the impurity being toluene-α-d_2. The chemical purity was greater than 99.5% by GPC.

Preparation of Phenylazotriphenylmethane

Phenylazotriphenylmethane (PAT) was prepared according to the procedure of Cohen and Wang (92). Preparation of N-phenyl-N'-tritylhydrazine proceeded smoothly, but oxidation of this hydrazine to the corresponding azo compound was frequently found to be incomplete. The oxidation was conducted by allowing a large excess of hydrogen peroxide in saturated aqueous sodium bicarbonate to react with an ethereal solution of the hydrazine. The degree of completeness of oxidation was followed by withdrawing a small portion of the ether layer and introducing anhydrous hydrogen chloride to the sample. The hydrazine hydrochloride was precipitated if oxidation was incomplete. When the ethereal solution was found to be free of the hydrazine, the PAT was isolated and recrystallized from a methylene chloride-ethanol mixture.

Specific examples appear below.

In a typical preparation of N-phenyl-N'-tritylhydrazine, 156 grams of triphenylchloromethane (0.56 mole) in 1500 ml ether were placed in a 3-liter flask equipped with reflux condenser, stirrer, and dropping funnel. Phenylhydrazine (111 ml, 1.12 mole) was added slowly during a period of one hour. The mixture was stirred five hours longer at room temperature, then filtered to remove the phenylhydrazine hydrochloride. The solvent was evaporated at reduced pressure. Recrystallization of the solid material from a methylene chloride-ethanol mixture produced 99 gm (0.28 mole, 50% yield) of N-phenyl-N'-tritylhydrazine, m. p. 125 - 132 °C (reported m. p. 134 - 135 °C).

N-Phenyl-N'-tritylhydrazine (99 gm) in 1800 ml of ether was stirred 6 hours at room temperature with 800 ml of saturated aqueous sodium bicarbonate and 58 ml of 30% hydrogen peroxide (70% excess). Treatment of a small sample of the ether solution with anhydrous hydrogen chloride resulted in the precipitation of a water-soluble hydrochloride. The ether layer was separated, washed once with 5% aqueous sodium sulfate and dried over the same salt. After removal of the solvent at reduced pressure the impure PAT was recrystallized from a methylene chloride-ethanol mixture and dried in a vacuum desiccator which was charged with paraffin shavings and calcium sulfate. The yellow crystals contained appreciable white material. The impure PAT (47 gm) was dissolved in 1000 ml of ether and stirred 10 hours at room temperature with 500 ml of saturated aqueous sodium bicarbonate and 40 ml of 30% hydrogen peroxide. The ether layer was washed and dried as before, then stirred five hours at room temperature with five grams of lead dioxide. The lead dioxide was removed by filtration and the solvent was evaporated at reduced pressure. During evaporation of the ether, the solution was cooled well below 0 °C by the loss of heat of vaporization. A mass of yellow crystals precipitated and was removed by filtratration. The remainder of the ether solution, about one-third of the original volume, was discarded. The crystals were dried at 2 mm pressure for 10 hours. The yield of PAT, m. p. 110 - 112 °C, was 24% (24 gm). Decomposition of a 0.096 M solution of this material in carbon tetrachloride at 60 °C gave yields of 5.7% benzene and 73.1% chlorobenzene. This material is listed as sample A in Table 1.

Sample B of PAT was used for the determination of reactivities toward the phenyl radical. It was prepared as follows. A solution of N-phenyl-N'-tritylhydrazine (180 gm) in 2000 ml of ether was stirred five hours at room temperature with 90 ml (50% excess) of 30% hydrogen peroxide in 1000 ml saturated aqueous sodium bicarbonate. The ether layer was washed once with 5% aqueous sodium hydroxide, twice with water, and filtered through anhydrous sodium sulfate. Treatment of a sample of the ether solution with anhydrous hydrogen chloride resulted in the formation of a water-soluble precipitate. The solvent was evaporated at reduced pressure. The crystals were washed with cold ethyl alcohol before recrystallization. Recrystallization from a mixture of methylene chloride and ethanol produced 93 gm of PAT, contaminated with white crystals. This material was treated as before with 90 ml of 30% hydrogen peroxide. The ether layer was washed and then dried over anhydrous sodium sulfate. Treatment of a small sample of the solution with anhydrous hydrogen chloride produced no cloudiness. Evaporation of the solvent at reduced pressure gave 78 gm of crude PAT. The azo compound was recrystallized from a mixture of methylene chloride and ethanol to give 60 gm (33% yield) of PAT, m. p. 111 - 112 °C (decomposition), after drying overnight at 2 mm pressure. The decomposition of a 0.096 M solution of this material in carbon tetrachloride at 60 °C resulted in yields of 5.4% benzene and 73.9% chlorobenzene. All samples of PAT were stored in a refrigerator at 5 °C. This material, sample B, Table 1, was decomposed at 60 °C in carbon tetrachloride after eight months' storage. The yields of benzene (5.4%) and chlorobenzene (73.5%) from the 0.096 M solution were unchanged within experimental error.

Sample C of PAT was prepared according to the following procedure. A solution of N-phenyl-N'-tritylhydrazine (80 gm) in 1500 ml of ether was stirred four hours at room temperature with 600 ml of saturated aqueous sodium bicarbonate solution and 30 ml of 30% hydrogen peroxide. At the end of this time additional 30% hydrogen peroxide (30 ml) was added and stirring was continued for six more hours. (A 110% excess of hydrogen peroxide was used.) The azo compound was isolated as previously described and recrystallized from a benzene-ethanol mixture. After drying overnight at 2 mm pressure, 28 grams of PAT (35% yield) were obtained, m. p. 110 - 112 °C. A solution of 2 gm of PAT, sample C, dissolved in 100 ml of ether became cloudy and a trace of hydrochloride precipitated when anhydrous hydrogen chloride was bubbled into the liquid for 10 minutes. In order to confirm the absence of benzene (recrystallization solvent) in sample C, a small portion (0.5 gm) of the PAT was dissolved in 20 ml carbon tetrachloride. The solvent was distilled under vacuum and examined by GPC. No benzene was detected. Decomposition of a 0.096 M solution of sample C in carbon tetrachloride at 60 °C gave yields of 7.2% benzene and 73% chlorobenzene (Table 1).

Sample D was prepared as follows. A solution of N-phenyl-N'-tritylhydrazine (21 gm) in 500 ml of ether was stirred at room temperature with 250 ml saturated sodium bicarbonate and 11 ml of 30% hydrogen peroxide for 2-1/2 hours. An additional quantity of 30% hydrogen peroxide (5 ml) was added, and stirring was continued for 2-1/2 hours longer. (A 100% excess of hydrogen peroxide was used.) The product was isolated as previously described. Recrystallization from a mixture of toluene and hexane produced 14 gm of impure PAT (66% yield) containing a large quantity of white crystals. This material, sample D, melted at 112 - 114 °C (decomposition) and complete decomposition of a 0.096 M solution in carbon tetrachloride at 60 °C resulted in yields of 18.1% benzene and 17.8% chlorobenzene. Treatment of 2.3 gm of sample D in 100 ml of ether with anhydrous hydrogen chloride gave a precipitate of 1.4 gm, which is equivalent to 55 mole per cent of N-phenyl-N'-tritylhydrazine if the formation of a mono-hydrochloride is assumed.

The melting points (decomposition) of various samples of PAT were in good agreement with the reported value of 110 - 112 °C. Melting point was found to be an extremely poor criterion of purity. Large quantities of the hydrazine mixed with the azo compound had a negligible effect on the melting point. Sample D of PAT, containing *ca*. 55% of the hydrazine, melted at 112 - 114 °C. Samples containing smaller quantities of the hydrazine melted at the same temperature as PAT. Hamilton (93) noted that a white crystalline impurity which had little effect on the melting point was usually obtained with the yellow PAT, and that the azo compound could not be further purified by repeated recrystallizations. Thus complete oxidation of the N-phenyl-N'-tritylhydrazine is essential.

For reasons given above the criteria of purity of PAT chosen for the present work were the amounts of benzene and chlorobenzene formed when the azo compound was decomposed in carbon tetrachloride. The PAT used throughout this study for the determination of reactivities was sample B, which yielded 0.054 mole benzene and 0.739 mole chlorobenzene per mole of PAT when a 0.096 M solution was completely decomposed in carbon tetrachloride at 60 °C. (Benzene value was the same by GPC and by ultraviolet absorption method.) The formation of benzene is not understood, and various treatments of the azo compound failed to eliminate benzene formation from PAT in carbon tetrachloride at 60 °C. A summary of these attempts appears in Table 1. (Procedure for decompositions and determination of products appear in a later section.)

Hydrogen chloride treatment of PAT

Anhydrous hydrogen chloride was bubbled for 10 minutes into 100 ml of anhydrous ether containing 2.3 gm of PAT. The solution was then filtered and the solvent evaporated at reduced pressure. The azo compound was dried under vacuum (2 mm) for several hours. Washing the ethereal solution with aqueous sodium bicarbonate was found to be unnecessary.

Silver nitrate treatment of PAT

Five grams of PAT were treated with silver nitrate according to the procedure of Overberger and DiGiulio (94). Reaction time was 46 hours and loss of the azo compound was appreciable. The yellow crystals were dried and decomposed in carbon tetrachloride without recrystallization.

Lead dioxide treatment of PAT

An ethereal solution of the azo compound (1 gm in 100 ml) was shaken with 2 gm of lead dioxide for one hour. The ether solution was dried and the solvent was removed at reduced pressure. The azo compound was dried under vacuum. Lead dioxide was used by Alder and Leffler (95) to insure complete oxidation of N-phenyl-N'-tritylhydrazine remaining in PAT.

Treatment of PAT with hydrogen peroxide in acetic acid

PAT (2 gm) in 100 ml glacial acetic acid was stirred at room temperature with 2 ml 30% hydrogen peroxide for seven hours. The solution was filtered, poured into a large excess of water and extracted three times with ether. After removal of the solvent the azo compound was recrystallized from methylene chloride-ethanol and dried. These conditions with a longer reaction time (several days) were used by Angeli (96) to convert azobenzene to azoxybenzene.

Efforts to treat PAT with molecular chlorine in carbon tetrachloride resulted in extensive destruction of the azo compound.

Table 20. Effects of various treatments on the decomposition products of 0.1 M PAT in carbon tetrachloride at 60 °C

PAT sample and treatment	Yields before treatment			Yields after treatment		
	C_6H_6[a]	C_6H_5Cl[a]	$\frac{C_6H_6}{C_6H_5Cl}$	C_6H_6[a]	C_6H_5Cl[a]	$\frac{C_6H_6}{C_6H_5Cl}$
A, none	0.057	0.731	0.078	-----	----	-----
B, none	0.054	0.739	0.073	-----	----	-----
D, HCl	0.181	0.178	1.02	0.053	0.72	0.074
C, HCl	0.072	0.73	0.099	0.056	0.74	0.076
C, $AgNO_3$	0.072	0.73	0.099	0.045	0.56	0.080
C, PbO_2	0.072	0.73	0.099	0.049	0.67	0.073
C, H_2O_2	0.072	0.73	0.099	0.052	0.71	0.073

[a] Mole/mole of PAT.

Decomposition Procedure for Competitive Reactions

A solution of carbon tetrachloride and the hydrogen-containing substrate was made by weighing each liquid to the nearest 0.2 mg in a glass-stoppered flask. PAT was then weighed into an ampoule of about 10 ml capacity, and enough of the solvent mixture was added to make the solution 0.096 M at room temperature. Solid compounds were weighed directly into the ampoule and the inside of the stem of the ampoule was washed with the carbon tetrachloride which was added volumetrically. The solution of azo compound was frozen in an acetone-"dry ice" slurry or in liquid nitrogen, evacuated to 1 - 2 mm, and thawed in order to remove gasses. The ampoule was then sealed while the frozen solution was maintained under vacuum. Gaseous substances were transferred to the ampoule, previously loaded with PAT and carbon tetrachloride, by means of a vacuum line equipped with a standard bulb of calibrated volume 0.578 liter. The pressure of the vapor in the standard bulb was measured by reading the difference in mercury levels of a manometer by means of a cathetometer. The ideal gas law was used in all cases to calculate the amount of material added. The sealed tubes were placed in an oil bath maintained at 60 ± 0.1 °C for slightly more than ten half-lives of PAT (4 hours). Ampoules were stored in a "dry ice"-acetone slurry until analyses were performed. Before gas chromatographic analysis each ampoule was broken and a solution of internal standard was added to the reaction mixture. The weighed solutions without PAT were checked by GPC for the presence of impurities which would interfere with determination of the products.

Procedure for Experiments under Oxygen Pressure

Decompositions under oxygen pressure were conducted in a Parr Pressure Reaction Apparatus. The azo compound and solvent were introduced into a thick walled pressure bottle which was wrapped with heating tape. After introduction of oxygen at the desired pressure the mixture was shaken mechanically and voltage was applied to the heater. About five minutes were required to raise the temperature to 60 °C. Temperatures were ready by a thermocouple which had been previously calibrated to include a correction for the temperature gradient across the glass wall of the reaction vessel. Temperature control was within ± 2 °C.

Methods for Quantitative Determination of Benzene and Chlorobenzene

Ultraviolet absorption method

Determination of benzene by ultraviolet absorption was useful in those reaction mixtures containing only substances easily separable from carbon tetrachloride by distillation. The procedure of Walling (18) was used. Carbon tetrachloride was accurately measured into the sample in such quantity as required to give an absorbance between 0.5 and 1.0. Carbon tetrachloride and benzene were codistilled and the absorbance at 262 mμ was measured. The molarity of benzene was obtained from a previously prepared calibration chart. The number of moles of benzene was calculated from the molarity on the basis of the total volume of carbon tetrachloride. Absorbance of the codistillate was found to be constant within one per cent up to 90% removal. In four instances identical pairs of reaction mixtures were analyzed for benzene by GPC and ultraviolet absorption. The two methods were found to agree within ± 1% relative error.

Gas phase chromatographic methods

A Perkin-Elmer Vapor Fractometer Model 154-D was used for all gas chromatographic work. Conditions used for gas chromatographic determination of benzene and chlorobenzene appear below. All columns were constructed of 1/4 inch O. D. metal tubing. Firebrick was treated with hexamethyldisilazane (97).

GPC conditions I Two columns were used in series. A 1-meter, 3,3'-oxydipropionitrile (ODPN) column (98), 20% by weight on 80/100 mesh firebrick, was followed by a 1-meter di-*n*-propyl tetrachlorophthalate column (99), 10% by weight on 80/100 mesh firebrick. Column temperature was 86 °C, and the rate of helium flow was 81 cc/min measured at ambient conditions.

GPC conditions II Two columns were used in series. The ODPN column described above was followed by a 2-meter

Perkin-Elmer column _A_.* Temperature was 86 °C, and helium flow rate was 112 cc/min.

GPC conditions III Two columns were used in series. A 1-meter _tris_-2-cyanoethoxypropane (TCEP) column, 20% by weight on 80/100 mesh firebrick, was followed by a 2-meter Perkin-Elmer column _A_. Temperature was 100 °C and helium flow rate was 104 cc/min.

GPC conditions IV Two 1-meter ODPN columns were used in series. Temperature was 78 °C and flow rate was 70 cc/min.

GPC conditions V Two 1-meter di-_n_-propyltetrachlorophthalate columns were used in series. Temperature was 86 °C, and helium flow rate was 45 cc/min.

GPC conditions VI A 2-meter Perkin-Elmer column _A_ was used at 100 °C with a helium flow rate of 100 cc/min (for chlorobenzene only).

GPC conditions VII Two 2.1-meter columns packed with "Silicone Rubber on Chromosorb Regular, 30/60 Mesh" from Wilkens Instrument and Research, Inc. were used at 76 °C with a helium flow rate of 80 cc/min (for chlorobenzene only).

Correction factors Correction factors given in Table 21 conform to the equation

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*Descriptive literature from the Perkin-Elmer Corporation describes this column as having a stationary phase of diisodecyl phthalate.

Moles A/Area A = (Moles B/Area B) x Correction Factor .

Gas chromatogram areas were measured with an Ott plainimeter. In several reaction mixtures tailing of one solvent was severe enough to necessitate a special correction factor. In such cases known quantities of internal standard and benzene or chlorobenzene were added to the same solvent mixture used for the reaction and the special factor was determined by GPC. Correction factors thus determined for chlorobenzene (A) - toluene (B) were 1.153 and 1.076 for solvents containing p-xylene and ethylbenzene respectively. The benzene (A) - toluene (B) correction factor used for the chloroform reaction was 1.20.

Table 21. Correction factors for GPC

Compound A	Compound B	Correction factor
Benzene	Toluene	1.08
Chlorobenzene	Toluene	0.98
Benzene	*sec*-Butylbenzene	1.18
Chlorobenzene	*sec*-Butylbenzene	1.07
Benzene	Chlorocyclohexane	1.06
Chlorobenzene	Chlorocyclohexane	0.98

Retention times A list of approximate retention times appears in Table 22, at the end of this section. With the exceptions of internal standards and reaction products, no effort was made to determine retention times accurately with very dilute samples. The specificity of some columns decreased after prolonged use. In these cases the retention time relative to benzene was used to place all retention times on the same basis. Compounds not eluted in thirty minutes are designated by N.E. With the exceptions of the first six compounds, the order is the same as that of Table 2. Retention times of several compounds not actually studied appear at the end of the table.

Side Reactions

Because of the formation of alkyl chlorides in competitive reactions between alkanes and carbon tetrachloride, it was necessary to insure that no peaks due to side products interfered with those of the products or standard on the gas chromatogram. This was accomplished by examining reaction mixtures by two or more combinations of gas chromatographic columns. It was found that changing from GPC conditions I to GPC conditions II displaced the retention times of alkyl chlorides relative to benzene by a factor of 1.3 to 1.4. In those cases which remained in doubt, the hydrocarbons were photochlorinated in order to obtain retention times of their chlorides. Details are summarized in Table 23.

Biphenyl had a retention time of 6.8 minutes in a 1-meter Perkin-Elmer column _O_ at 157 °C with a helium flow rate of 94 cc/min.* Reaction mixtures were randomly examined for the presence of biphenyl. All reactions under oxygen pressure were so examined. In no instance was biphenyl detected as a reaction product.

The colors of reaction mixtures deserve some comment. It has been noted (95) that unidentified decomposition products of PAT have a characteristic yellow color. Most reaction mixtures observed in the present study were pale red or yellow when first removed from the 60° bath. Upon cooling to room temperature the samples appeared to be clear yellow. This coloration persisted for several months, eventually fading. The reaction of triphenylmethane in carbon tetrachloride with PAT produced a deep red color which changed to pale yellow upon freezing at -78 °C and was regenerated upon warming to 20 °C. These color changes were repeated several times. The red color had faded considerably after twelve hours, and disappeared when air was introduced to the ampoule. It is noted that the triphenylmethyl radical

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*Descriptive literature from the Perkin-Elmer Corporation indicates that the stationary phase of column _O_ is silicone grease.

is attributed with a yellow color (47). Reactions with compounds containing nitrogen usually produced dirty red solutions often containing considerable solid material. The reaction with triphenylphosphine produced a large quantity of black precipitate.

The formation of chloroform was noticed to a small extent with some of the extremely reactive hydrocarbons such as triphenylmethane, and chloroform was detected in the reaction mixtures of di- and tri-phenylsilane. These reactions are believed to give chloroform by abstraction of a hydrogen atom by the trichloromethyl radical from a very reactive carbon-hydrogen bond. However, chloroform was formed by an independent path in reactions involving phosphine-carbon tetrachloride mixtures. Diphenylphosphine (5.75 mmoles) in carbon tetrachloride (42 mmoles) yielded <u>ca</u>. 6 mmoles of chloroform and formed a white precipitate when maintained at 60^{o} for 11 hours. A blank reaction mixture (without PAT) of 12 mmoles trimethylamine and 10 mmoles carbon tetrachloride, maintained four hours at 60^{0}, yielded 0.2 mmole of chloroform. The competition between trimethylamine and carbon tetrachloride for PAT produced no chloroform.

The reported (62) reaction between triphenylsilyl radical and chlorobenzene necessitated a control run to demonstrate that no chlorobenzene was so consumed under conditions similar to those of Reaction 107. 2,2'-Azobisisobutyronitrile (ABN, 0.23 mmole), triphenylsilane (3.8 mmoles), and chlorobenzene (0.91 mmole) in 4 ml carbon tetrachloride were maintained at 60° for 113 hours. Isobutyronitrile (0.2 mole/mole ABN) was detected by GPC, indicating that hydrogen abstraction at the Si-H bond had taken place to an appreciable extent. The amount of chlorobenzene remained unchanged as determined by GPC.

Reactions Involving Chlorides of Copper, Silicon, and Phosphorus

Copper (II) chloride

PAT (1.44 mmole) and copper (II) chloride (4.35 mole) in 15 ml isopropyl alcohol were maintained four hours at 60 °C. Although most of the copper (II) chloride dissolved, the mixture was not entirely homogeneous. The yield of chlorobenzene was 0.84 mole/mole PAT, and benzene was formed in yield of *ca*. 10%. The reaction was repeated on a larger scale in order to examine the inorganic precipitate formed. A solution of PAT (0.022 mole) and copper (II) chloride (0.067 mole) in 221 ml isopropyl alcohol was maintained at 60 °C for 6 hours under a nitrogen atmosphere in a 500 ml flask equipped with a reflux condenser. The only agitation was that provided by hand during the early stages of the reaction. A precipitate of white crystals (2.382 gm) was removed by filtration and stored under nitrogen in a vacuum dessicator. The material was insoluble in acetone, hexane, and benzene, but was soluble in pyridine. Hot water promoted a color change from white to red. Copper determination by titration with ethylenediaminetetraacetic acid in pyridine-water solution (azoxine indicator) showed that the precipitate contained 58% copper. The melting point was 421 - 423 °C, and organic impurities were observed to be present as evidenced by traces of material melting at ill-defined lower temperatures. Copper (I) chloride had the same solubility characteristics as the precipitate, and nantokite, Cu_2Cl_2, is white and melts at 422 °C. Copper (I) chloride contains 64.2% copper. Assuming the copper determination to be approximately correct (i.e., the error is due to organic impurities) results in a value of *ca*. 0.99 mole copper (I) chloride formed per mole of PAT decomposed.

A similar experiment with copper (II) methoxide yielded no anisole.

Silicon tetrachloride and phosphorus trichloride

Reaction mixtures of silicon tetrachloride and phosphorus trichloride were hydrolyzed before GPC examination. Solutions were cooled to 0 °C and hydrolyzed with chilled 5% aqueous sodium hydroxide (10% excess). The basic solution was added slowly through a reflux condenser while the flask containing the chloride was shaken. Upon completion of the hydrolysis, the inside of the condenser was washed with 10 ml water and 2 ml cyclohexane. After separation of layers, the aqueous phase was extracted with two 2 ml portions of cyclohexane. The organic fractions were combined and dried over anhydrous sodium sulfate for GPC analysis. (Carbon tetrachloride was used instead of cyclohexane when benzene was to be determined by ultraviolet absorption.) When the internal standard (toluene) was added before hydrolysis, examination of standard solutions in PCl_3 and $SiCl_4$ showed that the above procedure involved fractionation which gave rise to relative errors in the determinations of benzene and chlorobenzene of approximately -8% and +9% respectively. For reasons to be developed elsewhere it was determined that hydrolysis of phenyltrichlorosilane under these conditions did not give rise to benzene.

In most reactions of PAT with silicon tetrachloride, the solutions were colorless when taken from the oil bath and remained so at room temperature. Upon cooling to -78 °C, however, the reaction mixtures turned a bright red-orange color. The color seemed to develop initially above the level of the liquid and on the wall of the ampoule, as though colorless vapors were condensing to a red liquid. The color disappeared upon warming the mixtures to room temperature, and could be produced again by chilling to -78 °C. In one instance an attempt was made to trap the suspected gas. The contents of the ampoule were frozen in liquid nitrogen; the ampoule stem was broken and attached by means of glass tubing with a short rubber joint to a second clean ampoule. The liquid nitrogen was removed from the first ampoule and placed under the second. The contents of the first ampoule gradually warmed to room temperature, and a small quantity of rust colored frozen material appeared in the second ampoule. The second ampoule was attached to the vacuum line by means of a three inch length of rubber vacuum tubing, and evacuated while frozen. The stopcock to the pump was closed and the contents of the second ampoule were allowed to thaw at room temperature. Upon refreezing no red-orange coloration appeared. The second ampoule was sealed under vacuum while frozen. Upon warming this tube to room temperature it appeared to contain a small amount of liquid with some solid material, both colorless at all temperatures. The final contents were presumed to be silicon tetrachloride and silica.

Table 22. Relative retention times of selected compounds

Compound	GPC conditions	Retention time[a] (min.)
Carbon tetrachloride	I, II, III, IV, V	0.52, 0.66, 0.67, 0.43, 0.71
Benzene	I, II, III, IV, V	(1.0)
Toluene	I, II, III, IV, V, VII	1.84, 1.92, 1.82, 1.66, 2.16, 4.17
Chlorobenzene	I, II, III, IV, V, VII	3.78, 4.00, 3.67, 3.52, 4.32, 7.4
Chlorocyclohexane	I	3.04
sec-Butylbenzene	I	5.88
Dimethylpropane	I	0.12
Tetramethylbutane	I	0.36
Pentane	I	0.14
Hexane	I	0.18
Heptane	I	0.27
Octane	I, III	0.47, 1.02
Hexadecane	I	N.E.
2,2-Dimethylbutane	I	0.16
3-Methylpentane	I	0.16
2-Methylpentane	I	0.16

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[a] For conditions I, II, III, IV, and V retention times are relative to benzene. Actually observed retention times for benzene under the conditions specified in the text were 5.0, 6.4, 4.6, 7.9, and 5.2 minutes respectively.

Table 22. (Continued)

Compound	GPC conditions	Retention time[a] (min.)
3-Methylhexane	I	0.24
2,3-Dimethylbutane	I	0.16
2,4-Dimethylpentane	I	0.20
2,5-Dimethylhexane	I	0.32
2,2,3-Trimethylbutane	I	0.22
2,2,4-Trimethylpentane	I	0.26
2,2,5-Trimethylhexane	I	0.40
2,3,4-Trimethylpentane	I	0.40
Cyclopentane	I	0.18
Cyclohexane	I, II, IV	0.28, 0.50, 0.21
Cycloheptane	I, II	0.74, 1.2
Cyclooctane	I	1.58
Methylcyclopentane	I	0.22
Methylcyclohexane	I	0.38
cis-2-Butene	I	0.16
trans-2-Butene	I	0.16
2-Methyl-2-butene	I	0.18
2,3-Dimethyl-2-butene	I	0.26
1-Butene	I	0.12
1-Pentene	I	0.16
2-Pentene	I	0.16

Table 22. (Continued)

Compound	GPC conditions	Retention time[a] (min.)
1-Octene	I, II	0.64, *ca*. 1.25
2-Octene	I, II	0.64/0.74 (*cis*/*trans*), *ca*. 1.4
2-Methyl-1-butene	I	0.16
3-Methyl-1-butene	I	0.14
4-Methyl-2-pentene	I	0.18
Propene	I	0.12
2,3,3-Trimethyl-1-butene	I	0.24
3,3-Dimethyl-1-butene	I	0.16
1,3-Pentadiene	I	0.24
2-Phenylpropene	I, II	10.2, 11,1
1-Phenylpropene	I	13.4
Cyclopentene	I	0.24
Cyclohexene	I	0.44
3-Phenylpropene	I	6.1
2,5-Dimethyl-2,4-hexadiene	I	1.62
Propyne	I	0.14
1-Butyne	I	0.18
2-Butyne	I	0.26
t-Butylbenzene	I	>6
p-Chlorotoluene	I	*ca*. 6.6

Table 22. (Continued)

Compound	GPC conditions	Retention time[a] (min.)
m-Chlorotoluene	I	*ca.* 6.2
p-Phenoxytoluene	I	N.E.
p-Nitrotoluene	I	N.E.
p-Xylene	I, IV	3.8, 2.7
Mesitylene	I	6.8
Ethylbenzene	I, IV	3.3, 2.5
Cumene	I, IV, VII	4.3, 2.96, 12.3
Diphenylmethane	I	N.E.
Triphenylmethane	I	N.E.
Indan	I, II	11.8, 12.5
Tetralin	II	*ca.* 23
Hexamethylbenzene	I	N.E.
Biphenyl	I	N.E.
Triphenylamine	I	N.E.
Diphenyl ether	I	N.E.
Triphenylphosphine	I	N.E.
2-Picoline	I, II	5.6, 5.0
3-Picoline	I, II	10, 8.1
4-Picoline	I, II	10.4, 8.6
s-Collidine	I, II	14.2, >17
2,5-Dimethylpyrazine	I	N.E.

Table 22. (Continued)

Compound	GPC conditions	Retention time^a (min.)
2-Methylfuran	I	0.56
3-Methylthiophene	I	2.62
2-Methylthiophene	I	2.3
Di-2-thienylmethane	I	N.E.
Pyrrole	I	N.E.
N-Methylpyrrole	I	4.2
2,5-Dimethylpyrrole	I	N.E.
Trimethylamine	I	0.18
N,N-Dimethylaniline	I	N.E.
Thioanisole	I	N.E.
Methanol	I, V	0.6, 0.25
Dimethyl ether	I	0.14
Anisole	I	N.E.
Acetone	I, V	0.8, 0.35
3-Pentanone	I	1.97
Diisopropyl ketone	I	2.1
Acetic acid	I	N.E.
Methyl acetate	I, V	0.66, 0.37
Methyl benzoate	I	N.E.
Dimethyl malonate	I	N.E.
2,4-Pentanedione	I	8.80

Table 22. (Continued)

Compound	GPC conditions	Retention time[a] (min.)
Isobutyronitrile	I	2.66
Propionitrile	I	2.88
Acetonitrile	I	2.16
Tetramethylsilane	I	0.14
Phenyltrimethylsilane	I, V	5.2, 9.2
2-Nitropropane	I	4.8
Nitroethane	I	5.6
Nitromethane	I	4.8
Dimethyl sulfoxide	I	N.E.
Trichloromethane	I, II, III IV	0.84, 0.87, 0.87, 0.67
Dichloromethane	I	0.48
Chloromethane	I	0.16
Diphenylsilane	I	N.E.
Triphenylsilane	I	N.E.
Diphenyl amine	I	N.E.
Diphenylphosphine	I	N.E.
Fluorobenzene	I	1.1
α,α,α-Trifluorotoluene	I	1.04
p-Chloro-α,α,α-trifluorotoluene	I	2.62
Phenyl acetylene	I	6.6

Table 22. (Continued)

Compound	GPC conditions	Retention time[a] (min.)
Dioxane	I	2.8
Hexachloroethane	I	>6
Thiophene	I	1.3
Pyridine	I	*ca.* 5
Bromobenzene	I	*ca.* 7.6
Cyclohexanol	I	*ca.* 9.4
1-Chloro-2,2,3,3-tetramethylbutane	I	4.4
2-Chloro-2,3-dimethylbutane	I	1.00
1-Chloro-2,3-dimethylbutane	I	1.36
Chlorocyclopentane	I	1.50

Table 23. Conditions for analyses of competitive reactions

Reaction no.	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
1	Dimethylpropane	I	I	None detected
2	Tetramethylbutane	I	I	None detected
3	Pentane	I	I	None detected
4	Hexane	I	I	0.16
5	Heptane	I	I	0.13 (two)
6	Octane	I	III	0.04 + 0.07 + 0.05
7	Hexadecane	I	I	None detected
8	2,2-Dimethylbutane	II	II	0.03
9	3-Methylpentane	II	II	0.10 + 0.06
10	2-Methylpentane	II	II	0.14 + 0.04
11	3-Methylhexane	II	II	0.14 + 0.05 + 0.04
12	2,3-Dimethylbutane	II	II	0.27
13	2,4-Dimethylpentane	I	I	0.05 + 0.04
14	2,5-Dimethylhexane	I	I	0.23 (two)

Table 23. (Continued)

Reaction no.	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
15a	2,2,3-Trimethylbutane	U.V.	III	
15b	"	III	III, VI	0.15
16a	2,2,4-Trimethylpentane	I	V	
16b	"	U.V.	III	0.03
17a	2,2,5-Trimethylhexane	I	I	0.14
17b	"	I	VI	0.14
18	2,3,4-Trimethylpentane	I	III	0.07
19	Cyclopentane	I	I	0.1
20a	Cyclohexane	I	I	0.31
20b	"	I	I	0.28
20c	"	I	I	0.22
21	Cycloheptane	II	II	0.17 (?)
22a	Cyclooctane	U.V.	I	None detected
22b	"	I	I	None detected
23	Methylcyclopentane	I	I	0.07

Table 23. (Continued)

Reaction no.	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
24	Methylcyclohexane	I	I	0.15 + 0.13 + 0.09
25	*cis*-2-Butene	I	I	
26	*trans*-2-Butene	I	I	
27	2-Methyl-2-butene	I	I	
28	2,3-Dimethyl-2-butene	I	I	
29	1-Butene	I	I	
30	1-Pentene	I	I	
31	2-Pentene	I	I	
32	1-Octene	I	I	
33	2-Octene	I	I	
34	2-Methyl-1-butene	I	I	
35	3-Methyl-1-butene	I	I	
36	4-Methyl-2-pentene	I	I	
37	Propene	I	I	

Table 23. (Continued)

Reaction	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
38	2,3,3-Trimethyl-1-butene	I	I	
39	3,3-Dimethyl-1-butene	I	I	
40	1,3-Pentadiene	I	I	
41	2-Phenylpropene	I	I	
42	1-Phenylpropene	I	I	
43	Cyclopentene	I	I	
44	Cyclohexene	I	I	
45	3-Phenylpropene	II	II	
46	2,5-Dimethyl-2,4-hexadiene	I	I	
47	Propyne	I	I	
48	1-Butyne	I	I	
49	2-Butyne	I	I	
50	t-Butylbenzene	I	VI	
51	Toluene	U.V.	I	
52	p-Chlorotoluene	I	I	

Table 23. (Continued)

Reaction no.	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
53	m-Chlorotoluene	I	I	
54	p-Phenoxytoluene	I	I	
55a	p-Nitrotoluene	I	I	
55b	"	U.V.	I	
56	p-Xylene	IV	IV	
57	Mesitylene	I	I	
58	Ethylbenzene	IV	IV	
59	Cumene	IV	VII	
60	Diphenylmethane	I	I	
61	Triphenylmethane	I	I	0.1 mole $CHCl_3$/mole PAT
62	Indan	II	II	
63	Tetralin	II	II	
64	Hexamethylbenzene	I	I	
65	Biphenyl	I	I	
66	Triphenylamine	I	I	

Table 23. (Continued)

Reaction no.	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
67	Diphenyl ether	I	I	
68	Triphenylphosphine	I	I	0.13 mmole $CHCl_3$
69	3-Picoline	II	II	
70	4-Picoline	II	II	
71	s-Collidine	II	II	
72	2,5-Dimethylpyrazine	I	I	
73	2-Methylfuran	I	I	
74	3-Methylthiophene	I	I	
75	2-Methylthiophene	I	I	
76	Di-2-thienylmethane	I	I	
77	Pyrrole	I	I	
78	N-Methylpyrrole	I	I	
79	2,5-Dimethylpyrrole	I	I	
80	Trimethylamine	I	I	

Table 23. (Continued)

Reaction no.	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
81	N,N-Dimethylaniline	I	I	
82	Thioanisole	I	I	
83	Methanol	V	V	
84	Dimethyl ether	I	I	
85	Anisole	I	I	
86	Acetone	V	V	
87	3-Pentanone	I	I	
88	Diisopropyl ketone	I	I	
89	Acetic acid	I	I	
90	Methyl acetate	V	V	
91	Methyl benzoate	I	I	
92	Dimethyl malonate	I	I	
93	2,4-Pentanedione	I	I	
94	Isobutyronitrile	I	I	

Table 23. (Continued)

Reaction no.	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
95	Propionitrile	I	I	
96	Acetonitrile	I	I	
97	Tetramethylsilane	I	I	
98	Phenyltrimethylsilane	I	I	
99	2-Nitropropane	I	I	
100	Nitroethane	I	I	
101	Nitromethane	I	I	
102	Dimethyl sulfoxide	I	I	
103	Trichloromethane	I	I	
104	Dichloromethane	I	I	
105	Chloromethane	I	I	
106	Diphenylsilane	I	I	0.7 mole $CHCl_3$/mole PAT
107	Triphenylsilane	I	I	0.09 mole $CHCl_3$/mole PAT
108	Diphenylamine	I	I	

Table 23. (Continued)

Reaction no.	RH	Method of determination		Approximate yield of alkyl chloride(s) (mole/mole PAT)
		Benzene	Chlorobenzene	
109	Diphenylphosphine	I	I	1 mole $CHCl_3$/mole RH
110	Acetone-d_6	V	V	
111	Toluene-α-d_3			

SUMMARY

Techniques were developed for the determination of the products formed during the decomposition of phenylazotriphenylmethane in mixtures of carbon tetrachloride and various substances capable of donating hydrogen atoms to phenyl radicals. By the method of competitive reactions the relative reactivities of more than 100 compounds toward abstraction reactions by the phenyl radical were determined.

The reactivities toward the phenyl radical of primary, secondary, and tertiary carbon-hydrogen bonds in alkanes of simple structure were found to be 0.038 - 0.045, 0.36, and 1.78, respectively, relative to the rate of abstraction of chlorine from a single carbon-chlorine bond of carbon tetrachloride. Tertiary carbon-hydrogen bonds *beta* to quaternary or tertiary carbon atoms were found to be extremely unreactive toward phenyl radicals.

The primary, secondary, and tertiary allylic carbon-hydrogen bonds of alkenes were found to have reactivities of 0.57, 1.11, and 4.77, respectively. Crude estimates of the relative rates of addition of phenyl radicals to olefins were made from the data.

The relative reactivities of the α-carbon-hydrogen bonds of toluene, ethylbenzene, and cumene were determined as 0.36, 1.59, and 3.52, respectively. Studies of substituted

toluenes revealed no evidence for polar contributions to the transition state of the abstraction reaction.

From the relative rates of hydrogen abstraction at side-chains of heteroaromatic compounds, the following order of abilities of aromatic systems to stabilize arylmethyl radicals was established: 2-pyrryl > 2-thienyl > phenyl > 3-thienyl > 2-furyl > 2-pyrazyl > 2-, 3-, and 4-pyridyl.

The presence of a wide variety of functional groups adjacent to a carbon-hydrogen bond enhanced reactivity by a factor of four or less, with the exceptions of the amino and mercapto substituents, which had considerable activating abilities.

The reactivities of hydrogen atoms bonded to several heteroatoms were determined, and reaction of oxygen with phenyl radicals was studied. The primary deuterium isotope effect for abstraction reactions of the phenyl radical was determined.

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ACKNOWLEDGEMENTS

The author is very much indebted to Dr. Glen A. Russell for the suggestion of a problem and patient guidance throughout the course of this work.

Chemicals and equipment for this investigation were provided largely by the Chemistry Department of Iowa State University. The author is grateful to the department and to its employees, who have provided such excellent services in the procurement of materials and equipment.

Financial aid in the form of fellowships is gratefully acknowledged from the following agencies: Iowa State University Research Foundation (1959-60), National Science Foundation (1960-62), Procter and Gamble Company (1962), and Petroleum Research Fund (1962).

Significant contributions were made to this research by many members of the Russell group, who freely lent chemicals and equipment. The author is especially grateful to Dr. D. G. Hendry and Mr. J. D. Hunt for sharing their experience in vacuum line techniques, and to Mr. E. T. Strom for performing molecular orbital calculations. Many of the reactivities of compounds containing functional groups and heteroatoms were determined by Mr. Guy Griffin, a National Science Foundation Undergraduate Fellow from the University of Omaha.

The author is deeply grateful to his wife, Marcia, for

her patience and encouragement, and to Mr. and Mrs. F. F. Aggus for generous financial aid during a critical period.