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Reactivities of organic compounds toward phenyl radicals

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REACTIVITIES OF ORGANIC COMPOUNDS TOWARD PHENYL RADICALS

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INTRODUCTION

The primary objective of this work was to establish a comprehensive scale of the reactivities of hydrogen atoms α to common functional groups toward the phenyl radical. Because of the experimental difficulties involved in measuring absolute rates of radicals in solution, the method of competitive reactions is generally used in solving such problems (1). In the competitive method two compounds are allowed to compete for some reactive intermediate. 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 the measurement of either the disappearance of reactants or the appearance of products. In this work the appearance of products was measured by gas liquid chromatography (g.l.c.).

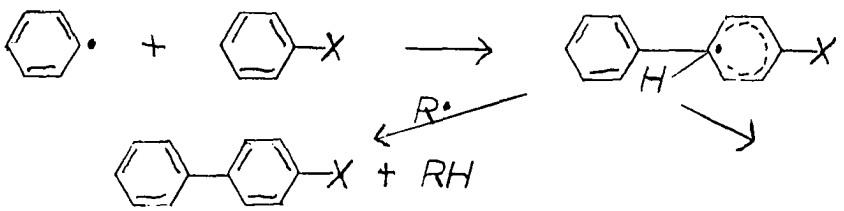
The data obtained have the form of relative rates or relative reactivities. By determining the relative rates of reaction of appropiate model compounds it is possible to arrive at conclusions regarding the influence of molecular structure on the reactivities of individual bonds. Comparisons can also be made with similar data for other radicals and conclusions drawn concerning the reactivities and selectivities of the radicals.

In the present work phenyl radicals were generated by the thermal decomposition of phenylazotriphenylmethane. The relative reactivities of more than 140 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: ZCH_3, ZCH_2R, Z_2CH_2, $ZCHR_2$, Z_3CH where Z = functional group and R = alkyl and/or aryl.

HISTORICAL

Earlier work with phenyl radicals concentrated almost entirely upon the addition of aryl radicals to aromatic systems. The literature of homolytic arylation has been reviewed (2-10) and may be represented by



The above equation represents the essential steps of the reaction. The aryl group usually enters predominantly at the ortho and para positions of substituted benzene regardless of the nature of the substituent X. Biphenyl resulting from the coupling of two phenyl radicals is seldom isolated as a product.

In the case of phenylazotriphenylmethane as a phenyl radical source, Eliel and coworkers (9) suggest that removal of the hydrogen atom from the phenylcyclohexadienyl radical is accomplished by the triphenylmethyl radical so that the RH compound in the above reaction is triphenylmethane. Moreover, in the presence of the triphenylmethyl radical dihydrobiphenyls or dihydroquatraphenyls are not important products.

Experiments (11, 12) with substituted aryl radicals show that the phenyl radical is a neutral species (no strong polarization) and its electronic demands in the transition state(s) should be about the same as those of an alkyl radical (3) except in those cases where the alkyl radical can act as an electron donor. At the present time the only investigation of abstraction reactions of the phenyl radical that has been

reported is that of Bridger and Russell (13). Since the present work is a continuation of Bridger's work no review will be made at this time, but the author will refer to Bridger's work throughout the results and discussion section whenever pertinent.

RESULTS AND DISCUSSION

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

$$Ph\text{-}N{=}N\text{-}CPh_3 \longrightarrow Ph\cdot + N_2 + Ph_3C\cdot \quad (1)$$

$$Ph\cdot + CCl_4 \xrightarrow{4k_{(Cl)}} PhCl + Cl_3C\cdot \quad (2)$$

$$Ph\cdot + RH \xrightarrow{\Sigma n_i k_{i(H)}} PhH + R\cdot \quad (3)$$

$$Ph_3C\cdot + Cl_3C\cdot + R\cdot \longrightarrow \text{Non-radical products}, \quad (4)$$

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 binetic expressions may be reduced to

$$\frac{\Sigma n_i k_{i(H)}}{4k_{(Cl)}} = \frac{(PhH)(CCl_4)}{(PhCl)(RH)} \quad (5)$$

Three assumptions are involved in the derivation of equation 5: (a) reactions 2 and 3 are each of the same molecularity in phenyl radical concentration and unimolecular in the concentration of substrate, (b) reactions 2 and 3 are the only source of benzene and chlorobenzene,

respectively, (c) the ratio of the carbon tetrachloride and the hydrogen-containing compound remains constant. Experimental tests of the three assumptions have been performed (13, 14) and the three assumptions shown to be correct for a limited number of substrates.

Equations 1 through 4 do not predict the formation of benzene during the decomposition of PAT in pure carbon tetrachloride. However, benzene is always formed in a low yield. The formation of benzene during decomposition of PAT in carbon tetrachloride has been discussed by Bridger (13, 14). In the previous work (14) on hydrogen abstraction reactions by phenyl radicals, the yield of benzene obtained experimentally from the decomposition of 0.1M PAT in carbon tetrachloride was corrected by subtracting 0.054 mole of benzene per mole of PAT. Therefore equation 5 after the correction becomes:

$$\frac{\Sigma n_i i_{i(H)}}{4k_{(cl)}} = \frac{(PhH - 0.054)(CCl_4)}{(PhCl)(RH)} \qquad (5')$$

The assumption that a correction of -0.054 is independent of solvent has been justified by the results of Bridger (14) but may be in error when the substrate is very reactive toward phenyl radicals.

The reactivities of a number of carbon-hydrogen bonds in compounds containing a functional group have been determined by using a standard technique which is described in detail in the experimental section. This technique simply involved the complete decomposition of a 0.1M solution of PAT in a mixture of the reference solvent, carbon tetrachloride, and the hydrogen containing compound at 60°C, followed by determination of benzene and chlorobenzene by g.l.c.

Definitions which will be used throughout this thesis are:

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 equation 5[1].

Because the volume of the reaction mixture remains constant mole ratios are used for carbon tetrachloride and the hydrogen-containing compound. Benzene and chlorobenzene yields are expressed as moles/mole PAT. When cosolvents are employed a correction, if necessary, has been made.

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.

3. Enhancement of reactivity is defined as reactivity per bond divided by the reactivity of an analogous carbon-hydrogen bond of an alkene.

The precision of the data varies somewhat, depending upon the reactivity of the compound under investigation. Errors may be magnified in the determination of reactivities per bond, which must be calculated from simultaneous equations involving total reactivities. Extremely unreactive compounds will give poor precision and in some cases satisfactory data could not be obtained. All data are summarized in tabular form in Table 1. The order of appearance is arbitrary, but is according to the various types of compounds containing functional groups and not according to the functional groups themselves.

Examination of Table 1 shows that the effects of functional groups are varied and in some cases surprising. Table 1 also shows that in many cases a cosolvent was also used. Since some solvents, especially

Table 1. Reactivities of compounds toward phenyl radicals at 60°C

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene[a]	Yield chlorobenzene[a]	Total reactivity[b]
1a	2-Methylpyrrole	0.207	0.536	0.112	0.8908
2a	3-Methylpyrrole	1.1516	0.1090	0.234	0.274
2b	" "	1.1516	0.0973	0.213	0.267
3a	1,2,5-Trimethylpyrrole	1.44	0.330	0.253	1.57
3b	" "	1.44	0.285	0.215	1.55
4a	3-Methylindole	6.538	0.505	0.442	6.67
5a	2-Methylindole	10.1	0.121	0.686	0.97
5b	" "	10.1	0.121	0.607	1.115
6a	N-Methylindole	1.461	0.071	0.261	0.095
6b	" "	1.461	0.067	0.259	0.073
7a	Indole	3.215	0.044	0.496	--
7b	"	3.215	0.051	0.545	--
8a	α-Methynaphthalene	0.8956	0.088	0.213	0.143
8b	" "	0.8956	0.111	0.218	0.234
9a	β-Methylnaphthalene	0.5299	0.0711	0.127	0.072
9b	" "	0.5299	0.0731	0.133	0.076
9c	" "	0.835	0.0706	0.181	0.0765
9d	" "	0.835	0.0664	0.179	0.058

[a] Mole/Mole PAT; $(PAT)_o = 0.1M$

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

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
10a	Trimethyl amine	0.4114	0.300	0.035	2.995
10b	" "	0.4114	0.229	0.025	2.960
11a	Dimethyl sulfide	1.0839	0.406	0.383	1.027
11b	" "	1.0839	0.400	0.391	0.990
12a	Dimethyl Disulfide	0.424	***	--	--
13a	Hexamethyldisilane	0.98	0.551	0.384	1.298
13b	" "	0.98	0.527	0.344	1.379
14a	Tetraphenyldimethyldisilane	28.607	0.057	0.661	--
14b	" " "	28.607	0.072	0.651	1.266
15a	Methyl silicate	0.6126	0.278	0.319	0.430
15b	" "	0.6126	0.331	0.314	0.540
16a	Hexamethyl siloxane	0.821	0.192	0.319	0.355
16b	" "	0.821	0.182	0.331	0.318
17a	Trimethyl phosphite	0.574	--	--	--[c]
18a	Trimethyl phosphate	0.398	0.058	0.653	--
18b	" "	0.398	0.081	0.671	0.016
19a	Dimethyl methylphosphonate	0.5178	0.966	0.543	0.0114
19b	" " "	0.5178	0.068	0.571	0.0127

[c]Michaelis-Arbuzov rearrangement occurred.

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
20a	Dimethyl sulfite	0.441	--	0.170	--
21a	2,3-Butanedione	1.54	0.066	0.348	0.053
21b	" "	1.54	0.076	0.326	0.104
22a	Acetophenone	0.2085	0.073	0.126	0.0331
22b	"	0.2085	0.057	0.139	--
23a	Methyl benzoate	0.2032	0.035	0.195	--[d]
24a	Dimethyl carbonate	0.343	0.119	0.514	0.0434
24b	" "	0.343	0.111	0.485	0.0403
25a	Dimethyl peroxide	0.992	0.140	0.522	0.185
26a	Azomethane	0.995	--	0.224	--[d]
26b	"	1.028	--	0.163	--
26c	"	1.076	--	0.230	--
27a	Methyl bromide	0.996	--	0.402	--[d]
27b	" "	1.0096	--	0.542	--
28a	Methyl iodide	0.479	--	--	--[e]
29a	Tetramethylcyclobutane-1,3-dione	1.352	0.344	0.180	2.178
29b	" " "	1.352	0.337	0.167	2.291

[d]Not enough benzene to measure.

[e]Only iodobenzene detected.

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
30a	2,2-Dimethylbenzodioxolane	0.6979	0.074	0.572	0.0244
30b	" "	0.6979	0.067	0.547	0.0166
31a	N-Methylphthalimide	1.401	--	--	--[d,f]
31b	" "	0.9485	0.111	0.163	0.645[g]
31c	" "	0.9485	0.094	0.167	0.537
32a	N,N-Dimethylbenzamide	0.8623	0.347	0.323	0.782[h]
32b	" "	0.8623	0.357	0.325	0.806
33a	Dimethylmercury	1.49	0.225	0.709	0.473
33b	"	1.49	0.1265	0.690	0.274
34a	Tetramethyltin	2.753	0.164	0.555	0.600
34b	"	2.753	0.132	0.555	0.441
35a	β-methylstyrene	1.153	0.099	0.122	0.425
35b	"	1.153	0.060	0.119	--
36a	Methylthiocyanate	0.9042	0.096	0.579	0.0656
36b	"	0.9042	0.100	0.601	0.0692
37a	Ethylmethyl sulfide	1.396	0.417	0.337	1.50
37b	" "	1.396	0.422	0.355	1.45

[f]Cosolvent pyridine added.

[g]Cosolvent dimethyl sulfoxide added and total reactivity corrected.

[h]Cosolvent bromobenzene added.

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
38a	Isopropylmethyl sulfide	1.0789	0.874	0.167	--
38b	" "	1.0789	0.896	0.168	--
39a	t-butylmethyl sulfide	1.1518	0.466	0.497	0.955
39b	" "	1.1518	0.465	0.496	0.954
40a	t-butylmethyl ether	0.7336	0.178	0.472	0.193
40b	" "	0.7336	0.178	0.482	0.189
41a	Diethyl sulfide	0.209	0.850	0.073	2.281
41b	" "	0.209	0.802	0.072	2.180
42a	Ethylphenyl sulfide	1.227	0.244	0.410	0.569
42b	" "	1.227	0.258	0.425	0.588
43a	Ethylphenyl ether	1.157	0.169	0.439	0.308
43b	" "	1.157	0.170	0.447	0.307
44a	Diethylether	0.7214	0.533	0.255	1.355
44b	"	0.7214	0.537	0.249	1.399
45a	Ethyl benzoate	0.733	0.086	0.402	0.0583
45b	" "	0.733	0.095	0.418	0.0719
46a	Diethyl sulfone	0.7834	0.325	0.410	0.518[h]
46b	" "	0.7834	0.355	0.457	0.516
47a	α-Ethylnaphthalene	0.4116	0.1969	0.1382	0.4819
47b	" "	0.4661	0.1904	0.1256	0.5061

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
48a	β-Ethylnaphthalene	0.5179	0.1885	0.1213	0.5743
48b	" "	0.5179	0.1849	0.1190	0.5693
49a	Ethyl thiocyanate	0.785	0.185	0.389	0.264
49b	" "	0.785	0.179	0.389	0.252
50a	Triethylamine	1.327	0.659	0.094	8.541[i]
50b	"	1.327	0.664	0.088	9.199
51a	Ethyl bromide	1.329	0.138	0.632	1.766
51b	" "	1.329	0.132	0.588	1.763
52a	Propiophenone	0.6474	0.329	0.266	0.669
52b	"	0.6474	0.300	0.255	0.625
53a	Diethylmercury	0.7934	0.318	0.053	3.95
53b	"	0.7934	0.315	0.055	3.77
54a	Isopropylbenzoate	1.038	0.088	0.444	0.0795
54b	" "	1.038	0.098	0.452	0.1010
55a	Isopropyl bromide	0.5005	0.295	0.339	0.356[j]
55b	" "	0.5005	0.296	0.372	0.326
56a	Isopropylphenyl ether	0.501	0.293	0.350	0.342
56b	" " "	0.501	0.277	0.339	0.330

[i]Chloroform detected.

[j]Bromobenzene detected.

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
57a	Isopropylphenyl sulfide	1.923	0.249	0.393	0.959
57b	" " "	1.923	0.263	0.437	0.918
58a	Di isopropyl sulfide	0.978	0.516	0.196	2.311
58b	" " "	0.978	0.508	0.198	2.243
59a	Di isopropyl disulfide	0.9982	0.233	0.436	1.049
59b	" " "	0.9982	0.244	0.394	2.015
60a	Di isopropyl ether	1.0328	0.467	0.215	1.981
60b	" " "	1.0328	0.476	0.238	1.812
61a	Di isopropyl sulfoxide	0.6378	0.227	0.436	0.251
61b	" " "	0.6378	0.226	0.394	0.278
62a	Isopropylphenyl ketone	1.000	0.168	0.381	0.299
62b	" "	1.000	0.167	0.375	0.301
63a	t-butyl alcohol	0.885	0.095	0.600	0.0604
63b	" "	0.885	0.096	0.613	0.0606
64a	Di-t-butyl peroxide	1.63	0.111	0.411	0.226
64b	" " "	1.63	0.113	0.412	0.233
65a	t-butyl chloride	2.50	0.082	0.610	0.115
65b	" "	2.50	0.081	0.620	0.109
66a	t-butyl bromide	1.071	0.095	0.415	0.106[j]
66b	" "	1.071	0.092	0.402	0.101
67a	t-butyl iodide	5.18	--	--	--[e]

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
68a	Trimethylacetic acid	0.867	0.090	0.568	0.055
68b	" "	0.867	0.092	0.580	0.057
69a	t-butylphenyl sulfide	3.93	0.073	0.392	0.191
69b	" "	3.93	0.076	0.400	0.216
70a	t-butylphenyl ether	0.478	0.094	0.438	0.0437
70b	" "	0.478	0.090	0.402	0.0428
71a	t-butyl benzoate	0.571	0.067	0.339	0.0219
71b	" "	0.571	0.069	0.342	0.0250
72a	Di-t-butyl disulfide	0.9059	0.165	0.408	0.248
72b	" "	0.9059	0.176	0.426	0.260
73a	Di-t-butyl sulfide	5.512	0.487	0.167	14.29
73b	" "	5.512	0.465	0.217	10.44
74a	β-t-butylnaphthalene	1.032	--	0.3034	--
75a	Dimethoxymethane	0.1470	0.549	0.190	0.383
75b	" "	0.1470	0.548	0.182	0.399
76a	S-trioxane	1.244	0.082	0.178	0.211[k]
76b	"	1.244	0.984	0.174	0.213
77a	1,4-pentadiene	0.9971	0.157	0.087	1.18
77b	" "	0.9965	0.158	0.087	1.19

[k]Cosolvent nitrobenzene added.

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
78a	Ethylene carbonate	0.7772	0.058	0.356	--[d,k]
79a	Methylene bromide	0.9657	0.132	0.058	1.30[j]
79b	" "	0.9657	0.134	0.054	1.43
80a	Dipnenoxymethane	0.720	0.097	0.384	0.081
80b	" "	0.720	0.106	0.384	0.098
81a	Dithiophenoxymethane	1.755	0.249	0.213	1.607[k]
81b	" "	1.755	0.254	0.215	1.633
82a	Malononitrile	0.6097	0.423	0.173	1.30[f]
82b	"	0.6097	0.424	0.174	1.30
83a	Ethylene oxide	1.10	--	--	--[d]
83b	" "	0.92	--	--	--
84a	1,3-Indanedione	3.401	0.170	0.397	0.741
84b	" "	3.401	0.164	0.336	0.855
85a	1,3-Diphenyl-1,3-Propanedione	1.229	0.041	0.107	--[d]
85b	" " "	1.229	0.067	0.107	0.149
86a	3-Pyrroline	7.951	0.416	0.290	9.925
86b	"	7.951	0.350	0.260	9.051
87a	Butadiene sulfone	0.8516	0.392	0.189	1.523
87b	" "	0.8516	0.329	0.157	1.492

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
88a	1,4-Thioxane	0.591	0.691	0.232	1.606
88b	" "	0.591	0.558	0.186	1.613
89a	Dioxane	0.999	0.446	0.404	0.997
89b	"	0.999	0.390	0.387	0.896
90a	N,N-Dimethylpiperazine	2.316	0.447	0.146	6.23
90b	" "	2.316	0.497	0.133	7.71
91a	1,3-Dioxolane	0.270	0.720	0.104	1.735
91b	" "	0.270	0.676	0.091	1.860
92a	Thioxanthene	6.324	0.248	0.239	5.186
92b	"	6.324	0.252	0.239	5.239
93a	Benzyl alcohol	1.170	0.397	0.308	1.303
93b	" "	1.170	0.396	0.314	1.274
93c	" "	0.6031	0.459	0.218	1.118
93d	" "	0.6031	0.467	0.209	1.192
94a	Benzyl bromide	1.231	0.122	0.199	0.421[j]
94b	" "	0.7247	0.144	0.136	0.4796
94c	" "	0.7247	0.138	0.130	0.4683
95a	Benzyl chloride	1.0686	0.272	0.422	0.552
95b	" "	1.0686	0.268	0.403	0.567
96a	Phenylacetic acid	1.528	0.165	0.334	0.5078
96b	" "	1.528	0.185	0.336	0.573

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
97a	Deoxy benzoin	2.882	0.162	0.388	0.802[k]
97b	" "	2.882	0.159	0.378	0.800
98a	N-benzylphthalimide	3.249	--	0.197	--[d,k]
99a	Dimethylbenzylamine	1.807	0.607	0.188	5.32
99b	" "	1.807	0.582	0.188	5.08
100a	1,3-Diphenylacetone	2.1345	0.366	0.369	1.815
100b	" "	2.1345	0.360	0.355	1.840
101a	Dibenzyl disulfide	4.027	0.086	0.152	0.848[k]
101b	" "	4.027	0.082	0.159	0.709
102a	Acenaphthene	2.367	0.296	0.154	3.72[k]
102b	"	2.367	0.289	0.151	3.68
103a	Anthrone	2.688	0.246	0.070	7.37[k]
103b	"	2.688	0.285	0.065	9.55
104a	Xanthene	3.043	0.538	0.118	12.48
104b	"	3.043	0.588	0.118	13.77
105a	Indene	1.533	0.242	0.109	2.64
105b	"	1.533	0.240	0.107	2.66
106a	Dibenzyl ether	0.8686	0.471	0.301	1.203
106b	" "	0.8686	0.450	0.300	1.147

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
107a	Neopentylbenzene	1.101	0.189	0.421	0.353
107b	" "	1.101	0.192	0.421	0.361
108a	Dibenzyl sulfide	3.615	0.374	0.389	2.974
108b	" "	3.615	0.376	0.395	2.947
109a	Benzyl benzoate	0.961	0.172	0.337	0.336
109b	" "	0.961	0.180	0.352	0.344
110a	Bibenzyl	4.339	0.180	0.538	1.016
110b	"	4.339	0.185	0.547	1.039
110c	"	5.264	0.161	0.564	0.976
110d	"	5.264	0.165	0.598	0.986
111a	Oxindole	1.827	0.135	0.083	1.782[k]
111b	"	1.827	0.104	0.075	1.220
112a	Phenylacetonitrile	0.8476	0.563	0.208	2.074
112b	" "	0.8476	0.555	0.199	2.134
112c	" "	0.981	0.574	0.218	2.34
113a	Allylbenzene	1.327	0.236	0.368	0.656
113b	"	1.327	0.230	0.358	0.652
114a	Phthalide	4.214	0.108	0.374	0.608[k]
114b	"	4.214	0.105	0.379	0.567
115a	Benzylphenyl ether	2.675	0.236	0.464	1.049
115b	" "	2.675	0.228	0.458	1.016

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
116a	9,10-Dihydroanthracene	2.23	0.436	0.0657	12.95
116b	" "	2.23	0.461	0.0602	15.10
117a	Fluorene	5.574	0.214	0.266	3.34[k]
117b	"	5.574	0.224	0.261	3.63
118a	Benzylphenyl sulfide	4.09	0.551	0.420	4.839
118b	" "	4.09	0.517	0.449	4.217
119a	Dibenzyl sulfoxide	3.371	0.138	0.201	1.409[f]
120a	1,1-Diphenylethane	2.67	0.287	0.372	1.672
120b	" "	2.67	0.276	0.368	1.611
121a	Diphenylacetonitrile	3.904	0.347	0.254	4.503[k]
121b	" "	3.904	0.359	0.272	4.380
122a	Benzal chloride	0.8942	0.428	0.279	1.199
122b	" "	0.8942	0.421	0.285	1.151
123a	Benzal bromide	1.4349	--	0.9311	--[j]
124a	2-Dienyl-1,3-dioxalane	1.5485	0.496	0.200	3.422
124b	" "	1.5485	0.448	0.201	3.035
125a	Cyclopentanone	0.8408	0.500	0.275	1.364
125b	" "	0.8408	0.533	0.279	1.410
126a	Tetrahydrofuran	0.9234	0.519	0.246	1.745
126b	" "	0.9234	0.495	0.257	1.585

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
127a	Thiphene	0.609	0.0509	0.418	--[d]
127b	"	0.609	0.0498	0.419	--
128a	Tetrahydrothiophene	0.6614	0.600	0.120	3.01
128b	" "	0.6614	0.600	0.115	3.14
129a	Pyrrolidene	--	--	--	--[i]
130a	1,1-Dichlorocyclopentane	0.8631	0.350	0.265	0.964
130b	" "	0.8631	0.364	0.261	1.025
131a	Tetramethylene sulfone	0.7944	0.195	0.465	0.241
131b	" "	0.7944	0.169	0.433	0.211
132a	Piperazine	3.075	0.226	0.141	3.75
132b	"	3.075	0.261	0.135	4.71
133a	Tetrahydropyran	0.8756	0.418	0.393	0.811
133b	" "	0.8756	0.392	0.381	0.777
134a	N-Methylmorpholine	2.25	0.551	0.210	5.325
134b	" "	2.25	0.530	0.214	5.004
135a	Morpholine	1.169	0.819	0.123	7.27[i]
135b	"	1.169	0.833	0.177	7.78
136a	Cyclohexanone	0.6887	0.581	0.290	1.251
136b	"	0.6887	0.581	0.281	1.315
137a	Piperidine	1.220	--	--	--[i]

Table 1. (continued)

Reaction number	Compound	$\frac{(CCl_4)}{(RH)}$	Yield benzene	Yield chlorobenzene	Total reactivity
138a	Pentamethylene sulfide	0.6565	0.658	0.197	2.013
138b	" "	0.6565	0.654	0.167	2.359
139a	1,4-Cyclohexandione	--	0.392	0.452	2.47[g]
139b	" "	--	0.378	0.454	2.28
140a	1,4-diozabicyclo(2,2,2)octane	5.488	0.159	0.231	2.495
140b	" " "	5.488	0.138	0.252	1.83
141a	N,N-Dimethylformamide	0.6738	0.416	0.455	0.536
141b	" "	0.6738	0.420	0.430	0.574
142a	Trimethylacetaldehyde	0.3351	0.825	0.041	6.301
142b	" "	0.3351	0.829	0.041	6.334
143a	Benzaldehyde	0.3781	0.502	0.088	1.924
143b	"	0.3781	0.500	0.086	1.960
144a	Methylformate	0.0881	0.378	0.249	0.115
144b	"	0.0881	0.380	0.241	0.119
145a	Tetraphenyldisilane	7.885	0.546	0.175	22.168
145b	" "	7.885	0.570	0.176	23.117
146a	Succimide	1.1448	0.212	0.5309	0.3407
146b	"	1.1448	0.2097	0.5316	0.3353
147a	Succinic	0.9538	0.2050	0.4899	0.2939
147b	Anhydride	0.9538	0.2118	0.4937	0.3048
148a	Benzal chloride/C_6H_{12}	4.409	Large	None	--[1]
149a	Benzyl chloride/C_6H_{12}	1.41	Large	None	--[1]

[1]See text.

aromatic compounds, have the ability to form π-complexes with free radicals, the effect of added cosolvent had to be investigated. Bridger (14) has shown that the relative rate constant for the abstraction of the benzylic hydrogen of toluene is independent of the toluene concentration indicating no solvent effect. The effect of adding aromatic solvents was investigated in the case of cyclohexane. The decomposition of 0.1M PAT at 60°C in a solution of 4.2M carbon tetrachloride, 4.3M cyclohexane and 1.15M 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 pyridine or bromobenzene gave a k_H/k_{Cl} value of 0.33±0.02 with a yield decrease of 6.6%. The value of k_H/k_{Cl} in the absence of aromatic solvents is 0.36. Therefore no strong 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 (15) observed that the benzyldimethylmethoxy radical in the presence of small amounts of cyclohexene reacts exclusively by β-elimination with no hydrogen abstraction taking place. These authors suggest the need for caution in interpretation of the results of competitive reactions involving olefins and alkoxy radicals.

The effects of various functional groups on the reactivities of α-carbon-hydrogen bonds toward phenyl radicals of compounds of the type $Z\text{-}CH_3$ where Z represents the functional group are summarized in Table 2. The reactivities of all carbon-hydrogen bonds were taken into account in the calculation of the relative reactivities of the α-carbon-hydrogen

Table 2. Effects of functional groups on reactivities of carbon-hydrogen bonds on compounds of the type $Z-CH_3$ toward the phenyl radical at 60°C

Compound	$Z-CH_3$ 100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X $k_{\alpha-H}/k_C$[c]	Relative $k_{\alpha-H}/k_C$
Neopentane	13.5[d]	0	13.5	1.17	1.00
Toluene	26.7[d]	0	26.7	8.90	7.6
Methyl chloride	7.0[d]	0	7.0	2.33	2.0
Methyl bromide	Low	0	Low	Low	Low
Trimethyl amine	298	0	298	33.1	28.3
Dimethyl sulfide	101	0	101	16.8	14.4
Thioanisole	37[d]	0	37	12.3	10.5
Dimethyl ether	27.4[d]	0	27.4	4.23	3.61
Anisole	9.1[d]	0	9.1	3.03	2.59
Acetone	17.6[d]	0	17.6	2.93	2.51

[a]Total reactvity from Table 1.

[b]Correction for beta or more remote carbon-hydrogen bonds if present, as explained in text.

[c]Reactivity of a single -carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d]From reference 14.

Table 2. (continued)

Compound	100 X total reactivity	Z-CH_3 Correction	100 X corrected reactivity	100 C $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
Acetophenone	3.33	0	3.33	1.11	0.95
Acetic acid	8.4[d]	0	8.4	2.8	2.39
Methylacetate	8.4[d]	8.4	Low	Low	Low
Methyl benzoate	0.01	0	Low	Low	Low
Acetonitrile	9.0[d]	0	9.0	3.0	2.56
Nitromethane	4.5[d]	0	4.5	1.5	1.28
Dimethyl sulfoxide	3.8[d]	0	3.8	0.63	0.54
N-Methylphthalimide	59.1	0	59.1	19.7	16.8
Tetramethylsilane	28.3[d]	0	28.3	2.36	2.02
Dimethyl peroxide	18.5	0	18.5	3.01	2.57
Dimethyl disulfide	Displacement	-	-	-	-
N,N-Dimethylbenzamide	79.2	0	79.2	13.4	11.45
α-Methylnaphthalene	18.8	0	18.8	6.27	5.36
β-Methylnaphthalene	7.06	0	7.06	2.35	2.01
Methylalcohol	13.3[d]	0	13.3	4.43	3.79

Table 2. (continued)

Compound	100 X total reactivity	Z-CH_3 Correction	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
Ethylbenzene	82.1	78.6	3.5	1.17	1.00
Methylthiocyanate	6.74	0	6.74	2.25	1.93
Dimethylmercury	37.4	0	37.4	6.23	5.31
Dimethylcarbonate	4.18	0	4.18	0.70	0.60
Azomethane	Very low				
Tetraphenyldimethyldisilane	126.6	0	126.6	21.1	18.1
Hexamethyldisilane	133.9	0	133.9	7.44	6.35
Tetramethyltin	52.0	0	52.0	4.33	3.7
β-Methylstyrene	42.5	0	42.5	14.17	12.1
2,3 Butanedione	8.8	0	8.8	1.47	1.26
Trimethyl phosphate	1.6	0	1.6	0.18	0.153
Hexamethyl siloxane	33.6	0	33.6	1.87	1.60
Methyl silicate	48.5	0	48.5	4.04	3.44
Phenyltrimethylsilane	20.0[d]	0	20.0	2.22	1.90
Dimethyl methylphosphonate	1.20	1.20	0	0	0

Table 2. (continued)

Compound	100 X total reactivity	Z-CH_3 Correction	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
N,N-Dimethylaniline	280.5[d]	0	280.5	46.7	40.0
Dimethyl sulfite	Low	0	Low	Low	Low
2-Methylpyrrole	89.08	0	89.08	29.69	25.4
3-Methylpyrrole	27.0	0	27.0	9.0	7.75
1,2,5-Trimethylpyrrole	156	156[d]	0	0	0
3-Methylindole	667	0	667	222	190
2-Methylindole	104	0	104	34.7	29.6
N-Methylindole	8.4	0	8.4	2.8	2.39

bonds. All carbon-hydrogen bonds in the beta or more remote positions were assigned the values Bridger (14) obtained from model alkanes which were k_H/k_{Cl} for primary equal to 0.038, secondary, 0.36; and tertiary, 1.78. These same values were also used for calculation of enhancements of secondary and tertiary 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 $k_H/k_{Cl} = 0.045$ for neopentane.

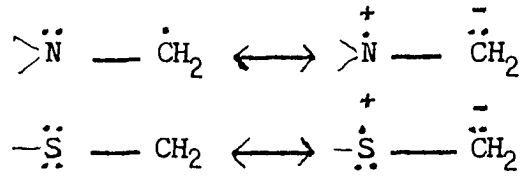
The enhancements listed in Table 2 are for the α-carbon-hydrogen bond only. The correction term is for all carbon-hydrogen bonds in the beta or more remote positions which must be calculated and then subtracted from the total reactivity of the compound. Also included in Table 2 are several of Bridger's results (14) which are used for comparison.

Reaction product studies of previous workers (16) have been relied upon to some extent in assigning reactivities, but enough compounds have been included in the present work that conclusions regarding the predominant site(s) of attack by phenyl radicals are largely independent of other workers. This is 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. These values lead to the conclusion that the methyl group attached to the oxygen in methyl acetate has a reactivity of zero, and that hydrogen abstraction takes place only at the methyl group attached to carbon. This also shows that no hydrogen abstraction occurs at the oxygen-hydrogen bond in acetic acid.

A similar result is obtained when comparing the reactivities of methanol and dimethyl ether. The total reactivities per carbon-hydrogen bond in this case are 0.0443 and 0.0423, respectively. Thus, it is concluded that no hydrogen abstraction occurs from the oxygen-hydrogen bond in methyl alcohol. A similar conclusion would be reached by comparison of the bond energies for carbon-hydrogen and oxygen-hydrogen. Wijnen (17) also determined the energy of activation for hydrogen abstraction by the methyl radical for methyl acetate in the gas phase. He commented that the energy of activation for abstraction reactions with acetic acid (18), methyl acetate (17), and acetone (19) were the same within experimental error. Bridger (14) has shown that for transfer reactions of the methyl and phenyl radicals, a general agreement exists between the two sets of data as to the effect of functional groups upon reactivity.

Inspection of Table 2 shows that the enhancement of reactivities of carbon-hydrogen bonds due to functional groups (relative $k_{\alpha\text{-H}}/k_C$ in the table) is not as great as is generally supposed. Exceptions are amines and sulfides. Generally speaking the enhancement of carbon-hydrogen bonds alpha to functional groups is less than fourfold as compared to their paraffinic counterparts. There are, however, some compounds to which no reasonable explanation can be given to account for their reactivity. One of these is N-Methylphthalimide. The enhancement here of 16.8 is somewhat surprising particularly in view of the fact that N-benzylphthalimide which should have a higher reactivity has in fact a very low reactivity (see Table 7). Tetraphenyldimethylsilane seems unusually high, 18.1, in comparison to the hexamethyldisilane rate enhancement of 6.35.

As shown in the table the phenyl and/or vinyl substituents activate about tenfold whereas the amino and sulfur substituents are more powerful activating groups. Both of these substituents presumably stabilize the incipient alkyl radical by resonance of the type;



The low yield of benzene observed for reaction of phenyl radical with dimethyldisulfide is consistent with the work of Pryor (20) who has shown that 98% displacement occurs with dimethyldisulfide.

$$C_6H_5\cdot + CH_3SSCH_3 \longrightarrow C_6H_5SCH_3 + CH_3S\cdot$$

Pryor observed only a very small amount of benzene whereas in the present work no benzene above that of the correction of 5.4% was observed.

The reactivities of the methyl-substituted heteroaromatics indicate that these reactivities can vary significantly and in a manner for which no explanation is immediately obvious.

The 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 (21).

The effects of various functional groups upon reactivities of α-carbon-hydrogen bonds toward the phenyl radical on compounds of the type $Z\text{-}CH_2\text{-}CH_3$ where Z represents the functional group are summarized in Table 3. Here again the reactivities of all carbon-hydrogen bonds were taken into account and the reactivities of beta or more remote positions were assigned values obtained by Bridger (14) who used model alkanes or

Table 3. Effects of functional groups on reactivities of carbon-hydrogen bonds on compounds of the type $Z\text{-}CH_2\text{-}CH_3$ toward the phenyl radical at 60°C

Compound	100 X total reactivity[a]	$Z\text{-}CH_2\text{-}CH_3$ Correction[b]	100 X corrected reactivity	100 X $k_{\alpha\text{-}H}/k_C$[c]	Relative $k_{\alpha\text{-}H}/k_C$
2,2-Dimethylbutane	29.5[d]	14.1	15.4	7.7	1.00
Ethylbenzene	82.1[d]	3.5	78.6	29.3	5.13
1-Butene	63.4[d]	3.5	59.9	29.95	3.9
Triethyl amine	877	10.5	866.5	144.4	18.8
Ethylphenyl sulfide	57.8	3.5	54.3	27.15	3.52
Diethyl sulfide	223	7.0	216	54	7.05
Methylethyl sulfide	147	53.3 (49.8+3.5)[e]	93.7	46.85	6.1
Diethyl ether	137.7	7.0	130.7	32.7	4.25
Ethylphenyl ether	30.8	3.5	27.3	13.7	1.75

[a]Average total reactivity from Table 1.

[b]Correction for beta or more remote carbon-hydrogen bonds if present as explained in text.

[c]Reactivity of a single α-carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d]From reference 14.

[e]3x16.6 + 3x1.17 = 53.3, from Table 2.

Table 3. (continued)

Compound	100 X total reactivity	$Z-CH_2-CH_3$ Correction	100 X corrected reactivity	100 X $k_{\alpha-H}/k_C$	Relative $k_{\alpha-H}/k_C$
Propiophenone	64.7	3.5	61.2	30.6	3.98
3-Pentanone	130[d]	7.0	123	30.75	4.0
Ethyl benzoate	6.51	3.5	3.01	1.5	0.2
Propionitrile	37.2[d]	3.5	33.7	16.85	2.19
Nitroethane	18.4[d]	3.5	14.9	7.45	0.97
α-Ethylnaphthalene	49.4	3.5	45.9	22.9	2.98
β-Ethylnaphthalene	57.1	3.5	53.6	26.8	3.5
Ethylthiocyanate	25.8	3.5	22.3	11.15	1.45
Diethylmercury	386	7.0	379	95	12.3
Ethyl bromide	176.4	3.5	172.9	86.45	11.2

since in this case the corrections were generally for a methyl group, the correction was obtained from the reactivity found for methyl-substituted functional groups as shown in Table 2. When this is done, it is noted by a subscript in the table.

Inspection of Table 3 again shows that enhancement of reactivity due to the functional group (relative $k_{\alpha\text{-H}}/k_C$ in the table) is not as great as generally supposed. Again the amines and sulfides are greater due to the resonance stabilization as discussed previously. Generally speaking the enhancement is fourfold or less with several unexplainable exceptions. Diethylmercury seems to give an enhancement which is high by a factor of 2 especially when compared to dimethylmercury (12.3 to 5.31). Ethyl bromide also has a high enhancement 11.2 when compared to methyl bromide whose enhancement was too low to measure. The reasons for these high enhancements are not known.

However several enhancements were within the range that one would expect. Ethyl benzoate with a very low enhancement (0.2) agrees very well with that found for methyl benzoate which was found to be also very low. Diethylsulfone with a fairly low enhancement would agree with the low radical stabilization factor (Q=0.15) found by Price and Gilbert (22).

The correction for methyl ethyl sulfide was supplied from Table 2 of 3x16.6 for the methyl group next to the sulfur and the 3x1.17 from Bridgers (14) values for a normal methyl group or in this case the methyl group next to the methylene group. Using this sort of a correction one finds that the enhancement of the α-carbon-hydrogen bonds for diethyl sulfide (7.05) and ethylmethyl sulfide (6.1) agree fairly well. However in the ethylphenyl sulfide (3.52) a factor of two exists as compared to

the diethyl sulfide. No apparent explanation can be supplied for this.

The effects of various functional groups upon reactivities of α-carbon-hydrogen bonds toward phenyl radicals in compounds of the type $Z\text{-}CH(CH_3)_2$ are summarized in Table 4. Again the reactivities of all carbon-hydrogen bonds were taken into account and the necessary correction applied for beta or more remote carbon-hydrogen bonds from either the model alkanes of Bridger (14) or from the data of previous tables.

Again from observation of Table 4 one finds that the rate enhancement due to the functional group on the α-carbon-hydrogen bond is fourfold or less. In the isopropyl case even for the sulfides one finds that the rate enhancement is not as high as was the case for methyl or ethyl substituted sulfides.

Comparison of Tables 2, 3 and 4 show that in general the enhancement of reactivity supplied by a functional group seems to decrease with increasing substitution at the alpha carbon. This is well defined for 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 the nitroalkane series is more severe going from 1.33 to 0.40 for the primary to the tertiary α-carbon-hydrogen bond. The sulfides show the same trend; 14.4 for dimethyl sulfide, 7.05 for diethyl sulfide, and only 2.01 for diesopropyl sulfide.

The steric factors discussed above seem to be general for free radical reactions for compounds containing functional groups. Data for reactions of the methyl radical (23) show that the reactivities of ethers

Table 4. Effects of functional groups on reactivities of carbon-hydrogen bonds on compounds of the type $Z\text{-}CH(CH_3)_2$ toward the phenyl radical at 60°C

Compound	100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X $k_{\alpha\text{-}H}/k_C$[c]	Relative $k_{\alpha\text{-}H}/k_C$
2,2,3-Trimethylbutane	71.0[d]	17.6	53.4	53.4	1.00
Cumene	93.3[d]	7.0	86.3	86.3	1.61
3-Methyl-1-butene	143[d]	7.0	136	136	2.55
Isopropyl bromide	34.1	7.0	27.1	27.1	0.51
Isopropylphenyl sulfide	93.8	7.0	86.8	86.8	1.62
Diisopropyl sulfide	227.7	14.0	213.7	106.85	2.01
Isopropylmethyl sulfide	High	--	--	--	--
Diisopropyl disulfide	153.2	14.0	139.2	69.6	1.3
Diisopropyl ether	189.7	14.0	175.7	87.85	1.64
Isopropylphenyl ether	33.6	7.0	27.6	27.6	0.52

[a]Average total reactivity from Table 1.

[b]Correction for beta or more remote carbon-hydrogen bonds if present as explained in text.

[c]Reactivity of a single α-carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d]From reference 14.

Table 4. (continued)

Compound	100 X total reactivity	Correction	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
Isopropylphenyl ketone	30.0	7.0	23.0	23.0	0.43
Diisopropyl ketone	120[d]	14.0	106.0	53.0	1.0
Isopropyl benzoate	9.02	7.0	7.02	7.02	0.13
Isobutyronitrile	73.0[d]	7.0	66.0	66.0	1.24
2-Nitropropane	24.4[d]	7.0	17.4	17.4	0.33
Diisopropyl sulfoxide	26.5	14.0	12.5	6.25	0.12

and alcohols decrease with increasing substitution at the alpha carbon. The trends are of the same order of magnitude with those observed for the phenyl radical.

Table 4 also shows that as expected from methyl and ethyl benzoate that isopropyl benzoate has a very low enhancement. Also the low enhancement of dimethyl sulfoxide 0.54 would predict a low enhancement of diisopropyl sulfoxide which was found to be 0.12.

The effects of various functional groups upon the reactivities of α-carbon-hydrogen bonds toward the phenyl radical upon compounds of the type $Z\text{-}C(CH_3)_3$ are summarized in Table 5. Here again the reactivities of all carbon-hydrogen bonds are taken into account and the corrections assigned are from either the model paraffinic compounds of Bridger (14) or from previous tables.

Examination of this type of compound shows that the α-carbon is fully substituted so that there are no α-carbon-hydrogen bonds available for attack by the phenyl radical. Therefore the only carbon-hydrogen bonds which are available for attack by the phenyl radical are beta to the functional group. One would expect that all other things being equal, that the functional group should have very little, if any, influence upon the reactivities of this type of compound.

Examination of Table 5 shows that this is generally the case. In fact for most cases the enhancement is less than 1.0 found for the model compound of this series, neopentane.

There are, however, upon examination of Table 5, several compounds which have relatively high enhancements. The most marked of these is di-t-butyl sulfide which has an abnormally high enhancement of 58.6.

Table 5. Effects of functional groups on reactivities of carbon-hydrogen bonds on compounds of the type $Z\text{-}C(CH_3)_3$ toward the phenyl radical at 60°C

Compound	100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X $k_{\alpha\text{-}H}/k_C$[c]	Relative $k_{\alpha\text{-}H}/k_C$
Neopentane	13.5[d]	0	13.5	1.17	1.00
2,2,3,3-Tetramethylbutane	20.2[d]	0	20.2	1.15	0.98
t-Butylbenzene	10.3[d]	0	10.3	1.14	0.97
t-Butylchloride	11.2	0	11.2	1.13	0.97
t-Butyl bromide	10.3	0	10.3	1.14	0.97
t-Butylphenyl sulfide	20.3	0	20.3	2.26	1.93
Di-t-butyl sulfide	1236	0	1236	68.5	58.6
t-Butylmethyl sulfide	95.5	50.4[e]	45.1	5.0	4.25
Di-t-butyldisulfide	25.4	0	25.4	1.41	1.20

[a]Average total reactivity from Table 1.

[b]Correction for beta or more remote carbon-hydrogen bonds, if present as explained in text.

[c]Reactivity of a single α-carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d]From reference 14.

[e]From Table 2.

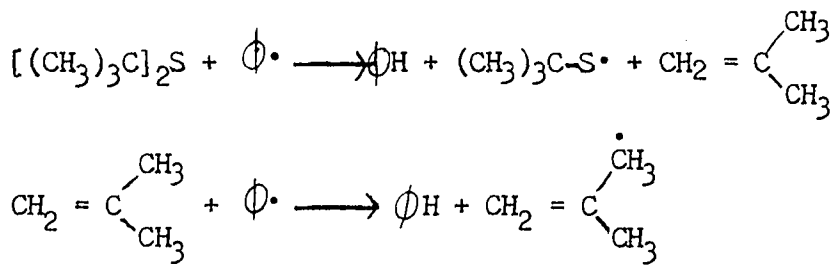
Table 5. (continued)

Compound	100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$[c]	Relative $k_{\alpha\text{-H}}/k_C$
t-Butylphenyl ether	4.33	0	4.33	0.48	0.41
t-Butylmethyl ether	19.1	12.7[e]	6.4	0.71	0.6
t-Butyl benzoate	2.35	0	2.35	0.26	0.22
Trimethylacetic	5.6	0	5.6	0.62	0.53
t-Butanol	6.05	0	6.05	0.67	0.57
Di-t-butyl peroxide	23.0	0	23.0	1.28	1.09
t-Butyl iodide	Low[f]	-	--	--	--
β-t-Butylnaphthalene	Low	-	--	--	--
Neopentylbenzene	35.7	25.2[g]	10.5	1.17	1.00

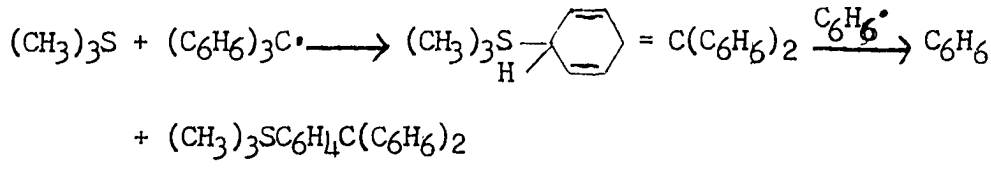
[f]Only iodobenzene detected; see text.

[g]From Table 7.

Substitution of one of the t-butyl groups by a methyl group decreases this enhancement to 4.25, while substitution of one t-butyl group by a phenyl group decreases the enhancement to only 1.93. These results seem to indicate that some sort of steric interaction must be involved to give the high enhancement for di-t-butyl sulfide. One possible explanation for this high enhancement could be a combination of hydrogen-abstraction and concerted elimination to give a reactive allyl system as pictured below:



The driving force for the concerted abstraction-elimination reaction may be the relief in steric strain. Note that such a steric driving force would be greatly reduced in methyl-t-butyl sulfide or phenyl-t-butyl sulfide. Also as shown the isobutenyl radical formed is a fairly reactive system stabilized by resonance stabilization which could account for an excess formation of benzene and consequently the high enhancement of di-t-butyl sulfide. Further support of this comes from the fact that a low boiling gaseous peak was found, but not identified, in the gas-chromatographs from this compound. Apparently, the t-butyl mercapto radical is consumed by reaction with the tiphenylmethyl radical since phenyl-t-butyl sulfide could not be detected by g.l.c. An additional complicating reaction might be,



$$(CH_3)_3S + (C_6H_6)_3C\cdot \longrightarrow (CH_3)_3S\text{-}C_6H_6\text{=}C(C_6H_6)_2 \xrightarrow{C_6H_6\cdot} C_6H_6$$

$$+ (CH_3)_3SC_6H_4C(C_6H_6)_2$$

Another problem is the fact that t-butyl mercaptan could also be present, and, if present even in small amounts, would provide a very reactive species for hydrogen abstraction by the penyl radical (note that di-t-butyl sulfide is only 97% pure, see experimental section).

Other effects noted from Table 5 are the fact that once again the ester t-butyl benzoate has a very low enhancement. This seems unusually low due to the fact that the carbon-hydrogen bond being attacked is beta to the functional group, in this case the alkyl-oxygen of an ester group. Also in the case of t-butyl iodide only iodobenzene was detected. In a typical experiment using a 1:1 CCl_4/RH molar ratio no benzene or chlorobenzene was detected. In the case of neopentyl benzene, the functional group considered here is the benzyl group rather than a phenyl group. The reactivities of the benzylic hydrogens are determined in a later table, Table 7.

The effects of functional groups on the reactivities of α-carbon-hydrogen bonds toward the phenyl radical on compounds of the type Z_2CH_2 are summarized in Table 6. Corrections due to other carbon-hydrogen bonds if present are calculated in a manner similar to that for other types of compounds as discussed previously.

In this table n-hexane is used as the model compound with which rate enhancements are compared for other functional group containing compounds. Examination of Table 6 and Table 2 shows that normally the

Table 6. Effects of functional groups on reactivities of carbon-hydrogen bonds on compounds of the type Z_2CH_2 toward the phenyl radical at 60°C

Compound	100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X k_{α}-H/k_C[c]	Relative k_{α}-H/k_C
Hexane[d]	79.8[e]	7.0	72.8	9.9	1.00
Diphenylmethane	140[e]	0	140	70	7.6
1,4-Pentadiene	118	0	118	59	6.5
Dichloromethane	47.2[e]	0	47.2	23.6	2.6
Dibromomethane	136	0	136	66	7.3
Dithiophenoxymethane	162	0	162	81	8.9
Diphenoxymethane	9.0	0	9.0	4.5	0.49
Dimethoxymethane	39.1	25.4[f]	13.7	6.85	0.75
S-trioxane	21.2	0	21.2	3.53	0.49

[a]Average total reactivity from Table 1.

[b]Correction for beta or more remote carbon-hydrogen bonds if present, as explained in text.

[c]Reactivity of a single α-carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d]Hexane used as reference compound for this series of compounds.

[e]From reference 14.

[f]From Table 2.

Table 6. (continued)

Compound	100 X total reactivity	Correction	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
Ethylene oxide	Low	--	--	--	--
Malononitrile	130	0	130	65	7.15
1,3-Diphenyl-1,3-propanedione	14.9	0	14.9	7.45	0.82
2,4-Pentanedione	47.1[e]	17.6[f]	29.5	14.75	1.62
Dimethyl malonate	18.0[e]	0	18.0	9.0	0.99

effect of disubstitution is not additive. The rate enhancement of toluene from Table 2 is 7.6 whereas that of addition of another phenyl group to give diphenylmethane remains at 7.6. Addition of a third phenyl group gives an enhancement of 7.3 (see Table 8). 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 2,4-pentanedione show an enhancement of only 1.62. Dimethyl ether shows an enhancement of 3.61 for its α-carbon-hydrogen bonds, but the disubstituted dimethoxymethane shows a rather low enhancement of only 0.75. Anisole shows an enhancement of 2.59 while the disubstituted compound diphenoxymethane shows an enhancement of 0.49. Thioanisole also exhibits the same sort of trend with an enhancement of 10.5 while its disubstituted derivative dithiophenoxy methane shows an enhancement of 8.9. Another pair of compounds which show no effects of disubstitution are acetophenone with an enhancement of 0.95 and 1,3-diphenyl-1,3-propanedione with an enhancement of 0.82.

The chloromethanes and the mono and disubstituted nitriles are exceptional in the respect that disubstitution is not additive. As shown in Table 2 methyl chloride has an enhancement of 2.0 while methylene chloride has an enhancement of 2.6 and from Table 8 chloroform has an enhancement of 6.8. It has been shown by Bridger (14) that no chlorine abstraction by the phenyl radical occurs with the chloromethanes. The abstraction reactions of methyl radicals with the chloromethanes are in general agreement with the results obtained by the phenyl radical study. However, the enhancement due to the proximity of chlorine seem to be greater in the reactions of the methyl radical. Acetonitrile shows an

enhancement of 2.56 while malononitrile shows the effect of disubstitution to be additive with an enhancement of 7.15. No immediate explanation can be offered for this at the present time.

The effects of various functional groups on the reactivities of α-carbon-hydrogen bonds toward the phenyl radical on compounds of the type $Z\text{-}CH_2\text{-}\phi$ are summarized in Table 7. Here again the reactivities of all carbon-hydrogen bonds were taken into account and the proper corrections applied either from Bridger's (14) model compounds or from previous tables. The interesting thing about this table is that the benzylic hydrogens are activated by the phenyl group to start with so that if the activation by a functional group is fourfold or less in alkyl type compounds as shown by previous tables, will the functional group have any effect upon benzylic carbon-hydrogen bonds.

Examination of Table 7 shows that in almost all cases the enhancement due to various functional groups is fourfold or less for these benzylic type compounds. Again there are notable exceptions, the major exceptions are again the amines and the sulfides. This is again expected due to the resonance stabilization character of nitrogen and sulfur as discussed earlier. Another exception is that of benzyl alcohol whose enhancement of 8.8 seems abnormally high. This value was taken from four reactions over a range where the CCl_4/RH molar ratio varied from 0.6 to 1.2. The same result was obtained each time. There is therefore no logical reason for this high enhancement, especially since the alkyl alcohols exhibit no abnormally high enhancement. Another major exception is that of phenylacetonitrile whose enhancement of 8.7 seems to be also abnormally high. The enhancement of acetonitrile was only 2.56 and that of the

Table 7. Effects of functional groups on reactivities of carbon-hydrogen bonds on compounds of the type Φ-CH_2Z toward the phenyl radical at 60°C

Compound	100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$[c]	Relative $k_{\alpha\text{-H}}/k_C$
Neopentylbenzene	35.7	10.5[d]	25.2	12.6	1.0
Ethylbenzene	82.1[e]	3.5	78.6	39.3	3.1
Diphenylmethane	140[e]	0	140	70	5.5
Allylbenzene	65.4	0	65.4	32.7	2.6
Toluene	26.7[e]	0	26.7	8.9	0.71
Benzyl chloride	56.0	0	56.0	28.0	2.22
Benzyl bromide	44.3	0	44.3	22.15	1.75
Benzyldimethyl amine	520	198.6[d]	321.4	160.7	12.7
Benzylphenyl sulfide	452.8	0	452.8	226.4	18.0

[a]Average total reactivity from Table 1.

[b]Correction for beta or more remote carbon-hydrogen bonds if present, as explained in text.

[c]Reactivity of a single α-carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d]From Table 2.

[e]From reference 14.

Table 7. (continued)

Compound	100 X total reactivity	Correction	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
Dibenzyl sulfide	296.1	0	296.1	74.3	5.9
Dibenzyl ether	117.5	0	117.5	29.4	2.3
Benzylphenyl ether	103.3	0	103.3	51.7	4.1
Deoxybenzoin	80.1	0	80.1	40.05	3.2
1,3-Diphenylacetone	182.8	0	182.8	45.7	3.7
Phenylacetic acid	54.0	0	54.0	27.0	2.14
Benzyl benzoate	34.0	0	34.0	17.0	1.35
Phenylacetonitrile	218.3	0	218.3	109.2	8.7
Benzyl alcohol	122.2	0	122.2	111.1	8.8
N-benzylphthalimide	Low	-	--	--	--
Dibenzyl disulfide	77.9	0	77.9	19.5	1.55
Bibenzyl	100.4	0	100.4	25.1	2.0
Dibenzyl sulfoxide	140.9	0	140.9	35.2	2.8

disubstituted compound malononitrile 7.15. The question is why should the phenylacetonitrile reactivity be enhanced to even a greater extent. The only possible explanation which has no experimental proof is the fact that somehow phenylacetonitrile tautomerizes to CH=C=N-H which could then have a very reactive nitrogen-hydrogen bond from which hydrogen abstraction could occur. This explanation, however, is completely unfounded and seems especially poor in view of the fact that diphenylacetonitrile has a normal enhancement of 2.7 as seen in Table 8. One would expect that diphenylacetonitrile would also have a high enhancement if the above explanation were true.

As was seen in previous Tables 2, 3 and 4 the methyl, ethyl and isopropyl benzoates all gave a decreased enhancement of reactivity, that is an enhancement of less than one. However, in the benzyl benzoate case the enhancement is not less than one and although the enhancement is small it is still greater than one (1.35). This was also not expected and no explanation is available.

Also notable at this time was that in the case of benzyl bromide approximately 61 per cent bromobenzene was detected by gas phase chromotography. This indicates that the primary reaction is that of bromine abstraction rather than hydrogen abstraction from the benzyl bromide or chlorine abstraction from carbon tetrachloride. Assuming that the bromine abstraction is an entirely separate reaction which does not interfere with hydrogen or chlorine abstraction reactions, the total reactivity can still be calculated to a high degree of accuracy. It should also be noted that no bromine abstraction was noted (no bromobenzene formed as detected by g.l.c.) with methyl bromide or ethyl bromide. However

for isopropyl bromide a small amount of bromine abstraction did take place as noted by bromobenzene formation and with t-butyl bromide, 27 per cent bromine abstraction took place. Bromobenzene was also detected for methylene bromide. As was the case of benzyl bromide, the total reactivity of the alkyl bromides was calculated only upon the hydrogen and chlorine abstraction reactions.

To test if any chlorine abstraction from benzyl chloride occurred a 1.41 molar ratio of benzyl chloride to cyclohexane was allowed to react with the phenyl radical. Only benzene was detected showing that no chlorine abstraction had taken place (no chlorobenzene was detected).

For dibenzyl sulfoxide a similar trend was observed as that for benzyl benzoate. In the alkyl series for sulfoxides the rate enhancement was decreased, that is less than one. For dimethylsulfoxide the enhancement was 0.54, for diisopropyl sulfoxide the enhancement was 0.12. However for the dibenzyl sulfoxide the rate enhancement was not decreased, but was increased by a factor of 2.8. There is no logical explanation for this, but one can still say that the functional group rate enhancement is less than fourfold in this case.

The effects of various functional groups on the reactivities of α-carbon-hydrogen bonds toward the phenyl radical on compounds of various types are summarized in Table 8. Here again corrections are made either from model compounds or from previous tables and in some cases both.

Compounds of the type Z_3CH, shown first in Table 8 have been discussed previously in discussing the effect of reactivity being or not being additive with di or trisubstitution. In this case 3-methylpentane was used for the model compound.

Table 8. Effects of functional groups on reactivities of carbon-hydrogen bonds toward the phenyl radical at 60°C

Compound	100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X k_{α}/k_C[c]	Relative k_{α}/k_C
Type Z_3CH					
3-Methylpentane	89.0[d]	41.2 (30.8+10.5)[e]	47.8	47.8	1.00
3-Methylhexane	107[d]	56.7 (46.2+10.5)[e]	40.3	40.3	0.85
Triphenylmethane	348[d]	0	348	348	7.3
Chloroform	326[d]	0	326	326	6.8
Type ΦCHZ_2					
Cumene	93.3	7.0	86.3	86.3	1.0
Toluene	26.7	0	26.7	8.9	0.103

[a] Average total reactivity from Table 1.

[b] Correction for beta or more remote carbon-hydrogen bonds if present, as explained in text.

[c] Reactivity of a single α-carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d] From reference 14.

[e] From Table 2 and Table 3.

Table 8. (continued)

Compound	100 X total reactivity	Correction	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
Benzylidine chloride	117.5	0	117.5	117.5	1.26
Benzylidine bromide	Bromine attack				
2-Phenyl-1,3-dioxalene	322	0	322	322	3.70
Type Φ_2CHZ					
1,1-Dipehnylethane	164.1	3.5	160.6	160.6	1.00
Diphenylmethane	140.0	0	140	140	0.85
Diphenylacetonitrile	444	0	444	444	2.7
Type Z-CHO					
N,N-Dimethylformamide	55.5	55.5	0	0	--
Trimethylacetaldehyde	631.8	10.5	621.3	621.3	--
Benzaldehyde	194.2	0	194.2	194.2	--
Methyl formate	11.7	0	11.7	11.7	--

For compounds of the type ϕCHZ_2 cumene is used as the model compound. In all cases these compounds exhibit a rate enhancement of fourfold or less. For benzal chloride there was no evidence of chlorine abstraction since a solution of benzal chloride and cyclohexane in the molar ratio of 4.409 gave no chlorobenzene upon reaction with the phenyl radical.

In the case of benzal bromide only bromobenzene was detected which indicates that only carbon-bromine bonds were attacked. Gas chromotography gave only the 5.4 per cent benzene which is the correction factor used for benzene as discussed previously, no chlorobenzene and a large amount of bromobenzene.

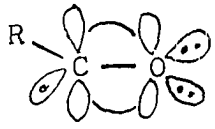
For compounds of the type $Z\text{-}CH\phi_2$ the rate enhancement is again normal being fourfold or less. However, due to the small number of compounds of this type, no real significant conclusions can be drawn. In this series 1,1-diphenyl ethane was used as the model compound.

For compounds of the type Z-CHO a variety of results was obtained. For dimethylformamide, after correcting for the six methyl hydrogens, one gets a reactivity of zero for the aldehyde carbon-hydrogen bond. But in the case of trimethylacetaldehyde one sees the very high reactivity of the aldehyde carbon-hydrogen bond of greater than 600. Benzaldehyde gives a much lower reactivity of about 200, a factor of 3 less than trimethylacetaldehyde while methyl formate gives a reactivity of the aldehyde type carbon-hydrogen bond of only 11.7.

Even though the functional group is varied in each of these cases, one would not expect the aldehyde carbon-hydrogen bond to vary from zero to 600. There was no reference compound used for this series so no rate

enhancement was calculated.

It seems rather obvious that conjugation between the oxygen or nitrogen atom and the carbonyl group in a formamide or formate decrease the stability of the formyl-type radical,



Note that in an aldehyde that the oxygen atom has formally only 6 electrons. However in resonance structures such as

$$\text{>N-CH=O} \longleftrightarrow \text{>}\overset{+}{\text{N}}\text{=CH-O}^{-}$$

the oxygen atom has formally 7 electrons with an increase in p-character of the oxygen orbitals. The resultant change in geometry of oxygen orbitals may have a profound effect in the stability of the formyl radical.

The effects of functional groups upon the reactivities of α-carbon-hydrogen bonds toward the phenyl radical on compounds which contain a five-membered ring are summarized in Table 9. Corrections which are used in this table were made from the reactivities of other compounds in the table. For example, the cyclopentanone correction of 41.6 is simply 4 x 10.4, the 10.4 being the reactivity of a normal carbon-hydrogen bond in a five-membered ring as found from cyclopentane. For 2-phenyl-1,3-dioxolane and 1,3-dioxolane the correction used was that for the reactivity found for tetrahydofuran.

Cyclopentane was used as the model compound in this table. Inspection of Table 9 shows once again that enhancement of α-carbon-hydrogen

Table 9. Effects of functional groups on reactivities of carbon-hydrogen bonds on compounds which contain a five-membered ring toward the phenyl radical at 60°C

Compound	100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$[c]	Relative $k_{\alpha\text{-H}}/k_C$
Cyclopentane	104[d]	0	104	10.4	1.00
Cyclopentanone	138.7	41.6	97.1	24.3	2.32
Tetrahydrofuran	166.5	41.6	124.9	31.2	3.00
Tetrahydrothiophene	308	41.6	266.4	66.6	6.4
Pyrrolidene	High (see text)				
Succimide	33.8	0	33.8	8.45	0.81
Succinic anhydride	29.3	0	29.3	7.3	0.70
Ethylene carbonate	Low	--	--	--	Low
Butadiene sulfone	150.7	0	150.7	37.7	3.62
Tetramethylene sulfone	26.6	41.6	--	--	Low

[a]Average total reactivity from Table 1.

[b]Correction for beta or more remote carbon-hydrogen bonds if present, as explained in text.

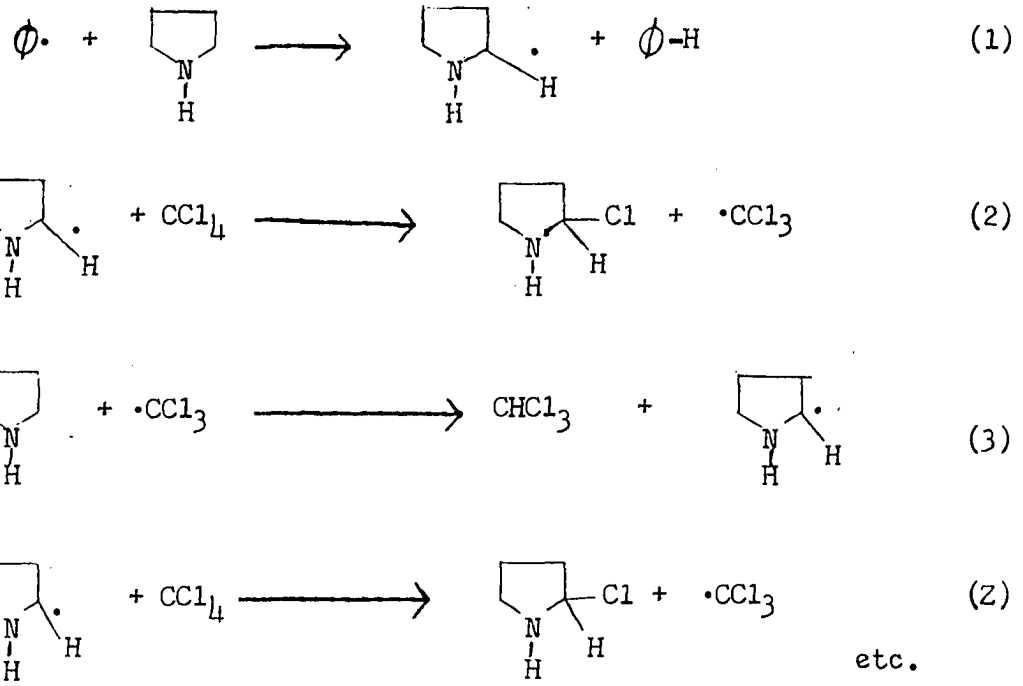
[c]Reactivity of a single α-carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d]From reference 14.

Table 9. (continued)

Compound	100 X total reactivity	Correction	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
3-Pyrroline	948	0	948	237	22.8
2-Phenyl-1,3-dioxolane	200	124.8 (4x31.2)	75.2	75.2	7.2
1,1-Dichlorocyclopentane	99.4	41.6	57.8	14.45	1.4
1,3-Dioxolane	179.7	124.8 (4x31.2)	54.9	27.45	2.64
Indane	317[d]	20.8	296.2	74.05	7.15
1,3-Indanedione	79.7	0	79.7	39.9	3.82
Indene	264	0	265	132.5	12.7
Fluorene	349	0	349	174.5	16.8
Acenaphthene	370	0	370	92.5	8.9
Oxindole	150.1	0	150.1	75.05	6.75
Phthalide	58.9	0	58.9	29.45	2.84

bonds is generally fourfold or less. The major exceptions to this are nitrogen and sulfur as expected due to the resonance stabilization which was discussed previously. Pyrrolidene in fact had a very high reactivity as evidenced by the large amount of benzene and the small amount of chlorobenzene formed and also a large amount of chloroform was formed. Chloroform could be presumably formed in the following manner in a



chain reaction if an extremely reactive carbon-hydrogen bond were present for reaction (3) to occur. The α-carbon-hydrogen bond must be reactive enough in reaction (3) to overcome the coupling reactions of either the trichloromethyl radical or the pyrrolidene radical with the trityl radical which is also present from the decomposition of PAT. To form the large amount of chloroform that was observed the reaction must be of the chain type pictured above and the phenyl radical is simply an initiator. To see if this was the case, an equimolar mixture of pyrollidene and carbon

tetrachloride were placed in a sealed tube with a trace of azobis isobutronitrile, AIBN, and allowed to react 6 hours at 60°C. Analysis by gas-chromotography showed a large amount of chloroform which shows that a chain reaction has occurred between the pyrrolidene and carbon-tetrachloride. An attempt was made to isolate the nitrogen-containing compound, but this failed. The chloropyrrolidene compound formed in reaction could possibly eliminate to give a dihydropyrrole, but this is not known. Although 3-pyrroline gave a high rate enhancement, no chloroform was observed for this compound.

The other compounds of Table 9 which have an enhancement of greater than four are all compounds which either have an allylic or benzylic hydrogen present. In both cases one would expect a higher rate enhancement. One should note also that the α-carbon-hydrogen bond of indane has a rate enhancement of 7.15 due to the delocalization of the electron by the aromatic system. However for indene which can delocalize the electron even better the enhancement increases to 12.7. Phthalide even though having benzylic carbon-hydrogen bonds gives an enhancement of only 2.84. However, this is consistent with the fact that, as seen from Tables 2, 3, 4 and 7, ester carbon-hydrogen bonds are extremely unreactive. From Table 7, it is seen that benzyl benzoate gave an enhancement of only 1.35 even though the benzylic carbon-hydrogen bonds are present.

The effects of functional groups on reactivities of carbon-hydrogen bonds toward the phenyl radical on compounds which contain a six-membered ring are summarized in Table 10. Here, as in Table 9, the corrections which are involved come from other compounds in the table or from previous

Table 10. Effects of functional groups on reactivities of carbon-hydrogen bonds on compounds containing a six-membered ring toward the phenyl radical at 60°C

Compound	100 X total reactivity[a]	Correction[b]	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$[c]	Relative $k_{\alpha\text{-H}}/k_C$
Cyclohexane	108[d]	0	108	9.0	1.00
Cyclohexanone	128.3	54 (6x9.0)	74.3	18.6	2.06
1,4-cyclohexadione	238	0	238	29.8	3.2
Dioxane	94.7	0	94.7	11.8	1.29
Tetrahydropyran	79.4	54	25.4	6.35	0.71
S-trioxane	21.2	0	21.2	3.53	0.39
Pentamethylene sulfide	218.6	54	164.6	41.15	4.6
N,N-Dimethylpiperazine	697	198.6[e]	498.4	62.3	6.9

[a]Average total reactivity from Table 1.

[b]Correction for beta or more remote carbon-hydrogen bonds, if present, as explained in text.

[c]Reactivity of a single α-carbon-hydrogen bond relative to a molecule of carbon tetrachloride.

[d]From reference 14.

[e]From Table 2.

Table 10. (continued)

Compound	100 X total reactivity	Correction	100 X corrected reactivity	100 X $k_{\alpha\text{-H}}/k_C$	Relative $k_{\alpha\text{-H}}/k_C$
Piperazine	423	0	423	54	6.0
1,4-Diazabicyclo[2,2,2]octane	216	0	216	18	2.0
N-Methylmorpholine	516	124.7 (3x33.1 + 4x6.35)	391.3	97.9[f]	10.9
Morpholine	752	25.4 (4x6.35)	726.6	181.7[f]	20.2
1,4-Thioxane	161	25.4 (4x6.35)	135.6	33.9[g]	3.8
Tetralin	490[d]	36	454	113.5	12.6
9,10-Dihydroanthracene	1402	0	1402	350.5	39.0
Xanthene	1308	0	1308	654	73
Thioxanthene	521.2	0	521.2	260.6	29
Anthrone	846	0	846	423	47
Piperidine	High (see text)				

[f]Carbon-hydrogen bonds alpha to nitrogen.

[g]Carbon-hydrogen bonds alpha to sulfur.

tables.

Here again the rate enhancement due to the functional group is generally fourfold or less. Also again the exceptions are the nitrogen and sulfur containing compounds which, as discussed previously, can stabilize the incipient radical. In the case of piperazine, morpholine, and N-methylmorpholine small amounts of chloroform were observed indicating that the chain reaction, which was discussed previously, had taken place to some extent. However with piperidene, a large amount of benzene and chloroform and a small amount of chlorobenzene were observed indicating that the chain reaction had occurred to a large extent.

The correction for cyclohexanone was made simply from the reactivity observed for cyclohexane of 9.0. Therefore for cyclohexanone the correction was 6x9.0. The same type of correction was used for tetrahydropyran and pentamethylene sulfide. For N, N-dimethylpiperazine the correction used was that obtained for methyl groups from trimethyl amine (see Table 2). In the morpholines the corrections were used from the reactivity observed for tetrahydropyran. The same correction was used for 1,4-thioxane.

As noted from Table 10, several compounds such as 9,10-dihydroanthracene, xanthene, thioxanthene, and anthrone have very high rate enhancements. The enhancement can not be due completely to the fact of resonance stabilization of the benzylic because on this scale toluene would have an enhancement of only one. This large variation from other compounds containing a six-membered ring could possibly be due to the fact that in these systems as the bond rupture occurs by the attack of the phenyl radical upon the carbon-hydrogen bond, the tetrahedral carbon

atom approaches a planar configuration. It may be possible that in rigid systems such as these that the planar configuration of the carbon atom would not only reflect relief of steric strain due to the decrease of non-bonded interactions, (β-strain (24, 25, 26)) but also reflect considerably more delocalization of the electron throughout the aromatic system. Bridger and Russell (13) have stated that the phenyl radical apparently gives rise to a transition state with sufficient bond breaking so that the relief in strain with the conversion of the tetrahedral carbon atom to the planar carbon atom is quite well developed, but without sufficient bond-breaking for extensive electron delocalization. This author feels that in the above cases, there is a combination of both electron delocalization and relief of strain in going from the tetrahedral to planar carbon, but to what extent each of these gives rise to the high rate enhancement observed is not known. There has been no other abstraction reactions using other radicals on these compounds with the exception of the work by Gregg and Mayo (27) who used fluorene and 9,10-dihydroanthracene as hydrocarbons for the chain transfer in the polymerization of styrene. However, no good comparisons can be made with the present data.

Other compounds listed in Table 1 but not listed or discussed in other tables include trimethyl phosphite. No reactivity could be obtained for this compound due to the fact that under the conditions employed for the phenyl radical reaction, the trimethyl phosphite reacts with carbon tetrachloride to give a Michaelis-Arbuzov rearrangement. This type of rearrangement is well known and has been well studied by Berlin and coworkers (28).

Another compound listed in Table 1 which has not been discussed is tetraphenyldisilane. Its high reactivity (k_H/k_{Cl} = 45.28) is fairly consistent with results obtained by Bridger (14) for triphenyl silane (k_H/k_{Cl} = 19.0) and for diphenylsilane (k_H/k_{Cl} = 15.4). This is also consistent with the observations of Curtice, Gilman and Hammond (29) who found that the chain transfer constant (styrene polymerization) of triphenylsilane to be much greater than that of the carbon analogue.

The only other compounds which are listed in Table 1 and not discussed are thiophene and indole. These compounds were run simply to make sure that no hydrogen abstraction had occurred on the ring. The results of both compounds showed that this was true, the only benzene which was formed was that formed in the decomposition of PAT itself.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Compounds studied in this work are grouped rather arbitrarily according to functional groups. The numbered order appearing in Table 1 will be 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 either 4,6 or 12 inches in length or a 16 inch spinning band column. Vacuum distillations were carried out on either the Vigreaux columns or on the spinning band column.

Solvents used for recrystallizing were generally reagent grade without any further purification.

Carbon tetrachloride was Mallinckrodt Reagent Grade and was passed through silica jel before use. Only the middle fraction was used from a fractionation carried out in a Todd Distillation Apparatus. Examination by gas phase chromotography (GPC) showed less than 0.1 mole per cent impurities.

2-Methylpyrrole was obtained from R. L. Hinman of Union Carbide Corporation. No impurities were detected by GPC.

3-Methylpyrrole was also obtained from R. L. Hinman of Union Carbide Corporation. No impurities were detected by GPC.

1,2,5-Trimethylpyrrole (Aldrich Chemical Company) showed no impurities by GPC and had the correct boiling point.

3-Methylindole (Aldrich Chemical Company) had the proper melting

point. No impurities were detected by GPC.

2-Methylindole (Aldrich Chemical Company) had the proper melting point. No impurities were detected by GPC.

N-Methylindole (Aldrich Chemical Company) was fractionated using the spinning band column. The middle fraction which was used showed greater than 99% purity by GPC.

Indole (Aldrich Chemical Company) showed no impurities by GPC.

α-Methylnaphthalene (Eastman Kodak Company) was distilled using a Vigreaux column. The fraction used showed no impurities by GPC.

β-Methylnaphthalene was obtained from Ashland Oil Company and was known to come from a non-petroleum source. It had the proper melting point and showed a purity of greater than 99% by GPC.

Trimethyl amine (Eastman Kodak Company) was anhydrous and the reaction run using a Stock type vacuum apparatus. The triethylamine was distilled three times from trap to trap before use. No GPC detection for purity was used.

Dimethyl sulfide (Phillips Petroleum Company) was distilled using the spinning band column. The fraction used showed greater than 99.8% purity by GPC.

Dimethyl disulfide (Phillips Petroleum Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Hexamethyldisilane (Dow Corning Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Tetraphenyldimethyldisilane was obtained from W. Atwell of Iowa

State University. It had the proper melting point and showed no impurities by GPC.

Methyl silicate was prepared by the method of Voronkov and Dolgov (30). The crude product was distilled using a Vigreaux column. The fraction used had a purity of greater than 97% by GPC.

Hexamethyl siloxane was prepared by the method of Sauer (31). Distillation from sodium was accomplished using a Vigreaux column. The fraction which was used showed no impurities by GPC.

Trimethyl phosphite (Virginia Chemical Company) was distilled using a spinning band column. The fraction used had a purity of greater than 96% by GPC.

Trimethyl phosphate (Virginia Chemical Company) was distilled using the spinning band column. The fraction used had a purity of greater than 98% by GPC.

Dimethyl methylphosphonate (Virginia Chemical Company) was distilled using a spinning band column. The fraction used had a purity of greater than 98% by GPC.

Dimethyl sulfite (Eastman Kodak Company) was distilled using a Vigreaux column. The fraction used had a purity of greater than 98% by GPC.

2,3-Butanedione (Eastman Kodak Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Acetophenone (Matheson, Coleman and Bell) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Methyl benzoate (Mallinckrodt Chemical Company) was distilled using Todd Distillation Apparatus. The fraction used showed no impurities

by GPC.

Dimethyl carbonate (Eastman Kodak Company) was distilled using a spinning band column. The fraction used showed greater than 99% purity by GPC.

Dimethyl peroxide was prepared by the method of Rieche (32). The compound had the correct boiling point and its refractive index matched that reported (32). The reaction was run in a sealed tube on a Stock-type vacuum apparatus and the peroxide was distilled three times from trap to trap on the vacuum apparatus before delivery to the tube used for the reaction.

Azomethane was prepared by the method of Thiele (33). The compound had the correct boiling point and was distilled three times in a Stock-type vacuum apparatus before use.

Methyl bromide (Eastman Kodak Company) was distilled from trap to trap on a Stock-type vacuum apparatus three times before use. Its purity appeared to be acceptable.

Methyl iodide (Matheson, Coleman, and Bell) was distilled using a spinning band column. The fraction used had a purity of greater than 98% by GPC.

Tetramethylcyclobutane-1,3-dione (Eastman Kodak Company) had the proper melting point and showed greater than 99% purity by GPC.

2,2-Dimethylbenzodioxolane was prepared by the method of Sloof (34). Boiling point, IR and an integrated NMR all supported the structure of the compound. Distillation from a Vigreaux column gave a fraction that showed to be greater than 99% pure by GPC.

N-Methylphthalimide (Eastman Kodak Company) had the proper melting

point. Examination by GPC showed greater than 99% purity.

N,N-Dimethylbenzamide (Eastman Kodak Company) upon recrystallization gave the proper melting point. The product used showed greater than 98% purity by GPC.

Dimethylmercury was prepared by the method of Gilman and Brown (35). Boiling point, IR and NMR all supported the structure of the compound. Distillation from a Vigreaux column gave a fraction that showed greater than 98% purity by GPC.

Tetramethyltin was prepared by the method of Jones et al. (36). Distillation of the crude product on a spinning band column gave a fraction which was used which showed greater than 99% purity by GPC.

β-Methylstyrene (Aldrich Chemical Company) was distilled using a spinning band column. The fraction used showed greater than 98% purity by GPC.

Methyl thiocyanate (Eastman Kodak Company) was distilled using a Vigreaux column. The fraction used showed greater than 97% purity by GPC.

Ethylmethyl sulfide (Eastman Kodak Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Isopropylmethyl sulfide (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

t-Butylmethyl sulfide (Aldrich Chemical Company) was distilled using a spinning band column. The fraction used showed greater than 97% purity by GPC.

t-Butylmethyl ether was prepared using a method similar to that reported by Ipatieff et al. (37). Distillation through a spinning band

gave a product whose structure was shown to be correct by IR and integrated NMR. The fraction used showed greater than 98% purity by GPC.

Diethyl sulfide (Phillips Petroleum Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Ethylphenyl sulfide was prepared by the method of Ipatieff et al. (37). Boiling point, IR and integrated NMR were all consistent with the structure of the compound. Distillation was accomplished on a Vigreaux column. The fraction used showed no impurities by GPC.

Ethylphenyl ether was prepared by a method similar to that used by Ipatieff et al. (37). Boiling point, IR and integrated NMR helped support the structure of the compound. Distillation through a Vigreaux column gave a fraction which showed no impurities by GPC.

Diethyl ether (Mallinckrodt Chemical Company) was distilled using a spinning band column. The fraction used showed greater than 99% purity by GPC.

Ethyl benzoate (Mallinckrodt Chemical Company) was distilled using a Vigreaux column. The fraction used showed no impurities by GPC.

Diethyl sulfone was prepared by the addition of 20 ml acetic acid and 20 ml hydrogen peroxide to 10 ml diethyl sulfide. This mixture was warmed on a steam bath for approximately one hour. The mixture was then cooled and scratched with the crystalline diethyl sulfone resulting. The crystals were then filtered and recrystallized to give a compound which showed greater than 99% purity by GPC.

α-Ehtylnaphthalene (Aldrich Chemical Company) showed greater than 99% purity by GPC.

β-Ethylnaphthalene (Aldrich Chemical Company) showed no impurities

by GPC.

Ethyl thiocyanate (Eastman Kodak Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Triethyl amine (Eastman Kodak Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Ethyl bromide (Matheson, Coleman and Bell) was distilled on a spinning band column. The fraction used showed greater than 99% purity by GPC.

Propiophenone (Matheson, Coleman and Bell) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Diethylmercury was prepared by the method of Gilman and Brown (35). Distillation of the crude material gave a fraction which showed greater than 98% purity by GPC. Boiling point, IR and NMR were consistent with the structure of the compound.

Isopropyl benzoate was prepared by allowing benzoic acid and isopropanol to react using a trace of concentrated sulfuric acid as a catalyst. The compound formed showed greater than 99% purity by GPC.

Isopropyl bromide (Matheson, Coleman and Bell) showed no impurities by GPC.

Isopropyl phenyl ether was prepared by a method similar to that of Ipatieff et al. (37). Boiling point, IR and integrated NMR confirmed the correct structure. Distillation was accomplished using a spinning band column. The fraction used showed greater than 99% purity by GPC.

Isopropylphenyl sulfide was prepared by a method similar to that of Ipatieff et al. (37). Boiling point, IR and integrated NMR confirmed the structure. Distillation was accomplished using a Vigreaux column. The

fraction used showed greater than 99% purity by GPC.

Diisopropyl sulfide (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Diisopropyl disulfide (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Diisopropyl ether (Aldrich Chemical Company) was distilled using a spinning band column. The fraction used showed no impurities by GPC.

Diisopropyl sulfoxide (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed no impurities by GPC.

Isopropylphenyl ketone was prepared by reaction of isopropyl Griguard with benzaldehyde followed by a $K_2Cr_2O_7$ oxidation. Distillation was accomplished using a Vigreaux column. The fraction used showed no impurities by GPC. Boiling point, IR and integrated NMR confirmed the structure of the compound.

t-Butanol (Matheson, Coleman and Bell) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Di-t-butyl peroxide (Matheson, Coleman and Bell) was distilled twice before using.

t-Butyl chloride was prepared from t-butanol and hydrochloric acid. Distillation was accomplished using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

t-Butyl bromide was prepared from t-butanol and red phosphorous and liquid Bromine. Distillation was accomplished using a Vigreaux column. The fraction used showed greater than 96% purity by GPC.

t-butyl iodide (Matheson, Coleman and Bell) was distilled using a Vigreaux column. The fraction used showed greater than 97% purity by GPC.

Trimethylacetic acid (Aldrich Chemical Company) was recrystallized before use. The compound showed greater than 99% purity by GPC.

t-Butylphenyl sulfide was prepared by the method of Ipatieff et al. (37). Distillation was accomplished using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

t-Butylphenyl ether was prepared by a method similar to that of Ipatieff et al. (37). Distillation was accomplished by a Vigreaux column. The fraction used showed greater than 97% purity by GPC.

t-Butyl benzoate was prepared by the method of Altschul (38). Distillation was accomplished using a Vigreaux column. The fraction used showed no impurities by GPC.

Di-t-butyl disulfide (Phillips Petroleum Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Di-t-butyl sulfide (Phillips Petroleum Company) was distilled using a Vigreaux column. The fraction used showed greater than 97% purity by GPC.

β-t-Butylnapthalene was prepared by the method of Crawford and Giesmann (39). The compound had the correct melting point, IR and NMR. The compound showed greater than 98% purity by GPC.

Dimethoxymethane (Eastman Kodak Company) was distilled using a spinning band column. The fraction used showed greater than 99% purity by GPC.

S-Trioxane (Aldrich Chemical Company) showed greater than 99% purity

by GPC.

1,4-Pentadiene (Eastman Kodak Company) was distilled three times from trap to trap on a Stock-type vacuum apparatus before using.

Ethylene carbonate (Aldrich Chemical Company) showed greater than 99% purity by GPC.

Methylene bromide (Matheson, Coleman and Bell) was distilled using a spinning band column. The fraction used showed greater than 98% purity by GPC.

Diphenoxymethane was prepared by the method of Bischoff and Frohlich (40). Distillation was accomplished using a Vigreaux column. Boiling point, IR and integrated NMR were consistent with the structure of the compound. The fraction used showed no impurities by GPC.

Dithiophenoxymethane was prepared by the method of Bischoff and Frohlich (40). IR and integrated NMR were consistent with the structure of the compound. GPC showed no impurities present in the compound.

Malononitrile (Aldrich Chemical Company) was distilled using a spinning band column. The fraction used showed no impurities by GPC.

Ethylene oxide was distilled three times from trap to trap in a Stock-type vacuum apparatus before using.

1,3-Indanedione (Aldrich Chemical Company) was recrystallized before using.

1,3-Diphenyl-1,3-Propanedione (Aldrich Chemical Company) was recrystallized before using.

Butadiene sulfone (Aldrich Chemical Company) was greater than 99% pure by GPC.

1,4-Thioxane (Aldrich Chemical Company) was greater than 98% pure

by GPC.

Dioxane (Matheson, Coleman and Bell) was purified by the method Hess and Frahm (41). Distillation was accomplished using a spinning band column. The fraction used showed no impurities by GPC.

N,N-Diemthylpiperazine (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

1,3-Dioxolane (Eastman Kodak Company) was distilled using a spinning band column. The fraction used showed greater than 99% purity by GPC.

Thioxanthene (Aldrich Chemical Company) was used as it was obtained.

Benzyl alcohol (Matheson, Coleman and Bell) was distilled using a spinning band column. The fraction used showed greater than 98% purity by GPC.

Benzyl bromide (Matheson, Coleman and Bell) was distilled using a Vigreaux column. The fraction used showed greater than 97% purity by GPC.

Benzyl chloride (Matheson, Coleman and Bell) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Phenylacetic acid (Eastman Kodak Company) was recrystallized before use.

Deoxybenzil (Eastman Kodak Company) was recrystallized before use.

N-benzylphthalimide was prepared by the method of Manske (42) and was used after two recrystallizations.

Dimethylbenzylamine (Eastman Kodak Company) was distilled using a spinning band column. The fraction used showed greater than 99% purity by GPC.

1,3-Diphenylacetone (Aldrich Chemical Company) was recrystallized

before use.

Dibenzyl disulfide (Aldrich Chemical Company) was recrystallized before use.

Acenaphthene (Aldrich Chemical Company) was recrystallized before use.

Anthrone (Aldrich Chemical Company) was recrystallized before use.

Xanthene (Aldrich Chemical Company) was recrystallized before use.

Indene (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Dibenzyl ether (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed no impurities by GPC.

Neopentylbenzene was prepared by the method of Bygden (43). Boiling point, IR and integrated NMR were consistent with the structure of the compound. Distillation was accomplished using a Vigreaux column. The fraction used showed no impurities by GPC.

Dibenzyl sulfide (Aldrich Chemical Company) was recrystallized before use.

Benzyl benzoate (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed a purity of greater than 98% by GPC.

Bibenzyl (Eastman Kodak Company) was recrystallized before use.

Oxindole (Aldrich Chemical Company) was recrystallized before use.

Phenylacetonitrile (Aldrich Chemical Company) was recrystallized before use.

Allylbenzene (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Phthalide (Aldrich Chemical Company) was recrystallized before use.

Benzylphenyl ether was prepared by the method of Ipatieff et al. (37) and had the proper boiling point melting point, IR and NMR. The fraction used showed greater than 99% purity by GPC.

Fluorene (Aldrich Chemical Company) was recrystallized before use.

Benzylphenyl sulfide (Aldrich Chemical Company) was recrystallized before use.

Bibenzyl sulfoxide (Aldrich Chemical Company) was recrystallized before use.

1,1-Diphenylethane was prepared by addition of phenyl Griguard to acetophenone. The resulting alcohol was eliminated with acid and the olefin then hydrogenated using Platinum as a catalyst. Distillation was accomplished using a Vigreaux column. Boiling point, IR and integrated NMR proved the structure to be correct. The fraction used had a purity of greater than 98% by GPC.

Diphenylacetonitrile (Eastman Kodak Company) was recrystallized before use.

Benzal chloride (Eastman Kodak Company) was distilled using a Vigreaux column. The fraction used had greater than 99% purity by GPC.

Benzal bromide was prepared by the method of Closs and Moss (44). IR and NMR were consistent with the structure of the compound. GPC showed no impurities in the compound.

2-Phenyl-1,3-dioxolane was prepared by the method of Hibbert and Timm (45). Boiling point, IR and integrated NMR were consistent with the structure of the compound. A Vigreaux column was used for the distillation and the fraction used showed greater than 97% purity by GPC.

Cyclopentanone (Arapahoe Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Tetrahydrofuran was purified by the method of Fieser (46). It was distilled using a spinning band column. The fraction used showed greater than 98% purity by GPC.

Thiophene (Eastman Kodak Company) was distilled using a spinning band column. The fraction used showed greater than 99% purity by GPC.

Tetrahydrothiophene (Eastman Kodak Company) was distilled using a spinning band column. The fraction used showed greater than 98% purity by GPC.

Pyrrolidene (Eastman Kodak Company) showed greater than 99% purity by GPC.

1,1-Dichlorocyclopentane was prepared by the method of Braude and Forbes (47). Boiling point, KR and integrated NMR were consistent with the structure of the compound. Distillation was accomplished using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Tetramethylene sulfone (Aldrich Chemical Compnay) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Piperazine (Aldrich Chemical Company) showed greater than 99% purity by GPC.

Tetrahydropyran (Aldrich Chemical Company) was distilled using a spinning band column. The fraction used showed greater than 99% purity by GPC.

N-Methylmorpholine (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity

by GPC.

Morpholine (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 97% purity by GPC.

Cyclohexanone (Matheson, Coleman and Bell) was distilled using a spinning band column. The fraction used showed greater than 99% purity by GPC.

Piperadine (Matheson, Coleman and Bell) showed greater than 99% purity by GPC.

Pentamethylene sulfide (Aldrich Chemical Company) showed greater than 98% purity by GPC.

1,4-cyclohexandione (Eastman Kodak Company) was recrystallized before using.

1,4-Diozabicyclo[2,2,2]octane (Houdry Process Corrporation) was recrystallized and the reaction mixture weighted in a dry box.

N,N-Dimethylformamide (Matheson, Coleman and Bell) was purified according to the procedure of Fieser (46). It was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Trimethylacetaldehyde (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity by GPC.

Benzaldehyde (Matheson, Coleman and Bell) was distilled using a Vigreaux column. The fraction used showed greater than 99% purity by GPC.

Methyl formate (Aldrich Chemical Company) was distilled using a Vigreaux column. The fraction used showed greater than 98% purity.

Tetraphenyldisilane was given to the author by W. H. Atwell of Iowa

State University and had the proper melting point, IR and NMR spectra.

Succimide (Eastman Kodak Company) was recrystallized before using.

Succinic anhydride (Eastman Kodak Company) was recrystallized before using.

The above compounds which were checked for purity by GPC were injected neat if a liquid or dissolved in a suitable solvent if a solid. Low boiling liquids were checked for purity on the columns used for benzene and chlorobenzene detection, while high boiling liquids and solids were checked using high temperature columns.

Preparation of phenylazotriphenylmethane

Phenylazotriphenylmethane (PAT) was prepared according to the procedure of Cohan and Wang (48). Preparation of N-phenyl-N'-tritylhydrazine proceeded smoothly, but oxidation of this hydrazine to the azo compound was more difficult. The oxidation was accomplished by oxidizing with a large excess of hydrogen peroxide in saturated aqueous sodium bicarbonate and an etheral solution of the hydrazine. In several preparations, this procedure had to be repeated two, three or four times before the oxidation was complete. A specific example appears below.

In a typical preparation of N-phenyl-N'-tritylhydrazine, 0.5 mole of triphenylchloromethane in 1500 ml ether were placed in a 3-liter flask equipped with reflux condenser, stirrer and dropping funnel. One mole of phenylhydrazine was added slowly through the period of one hour. The mixture was then stirred five hours longer at room temperature, then filtered to remove the phenylhydrazine hydrochloride. The solvent was then evaporated at reduced pressure. Recrystallization of the solid

material from a methylene chloride-ethanol mixture produced 0.25 mole of N-phenyl-N'-tritylhydrazine, m.p. 128-130°C (reported m.p. 134-135°C).

N-phenyl-N'-tritylhydrazine (0.25 mole) 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). The ether layer was separated, washed with 5% aqueous sodium sulfate and dried over sodium sulfate. After removal of the solvent at reduced pressure, the resulting PAT was redissolved in 1800 ml of ether and fresh saturated aqueous sodium bicarbonate and hydrogen peroxide added and the process repeated. This process was repeated either two, three or four times until decomposition of a 0.096M solution in carbon tetrachloride at 60°C gave in a typical example 5.5% benzene and 82.5% chlorobenzene. The yield of PAT in the above example was 0.05 mole with a m.p. 111-112°C (reported m.p. 110-112°C).

Bridger (14) tried various types of oxidation procedures to try to get the yield of benzene less than 5.4% upon decomposition in carbon tetrachloride. One further method was tried by this worker.

Active manganese dioxide was prepared by the method of AHenburrow (49) and a large excess stirred with an etheral solution of PAT for 24 hours. After filtration of the manganese dioxide and removal of the solvent at reduced pressure, decomposition of the PAT in carbon tetrachloride gave no change in the benzene and chlorobenzene produced. The melting point of PAT after this procedure was also unaffected.

Decomposition Procedure for Competitive Reactions

A solution of carbon tetrachloride and the hydrogen-containing substrate was made by weighing each to the nearest 0.2 mg in either a glass or cork stoppered vial. PAT was then weighed into an ampoule of about 10 ml capacity, and enough of the solvent mixture added to make the solution 0.096M at room temperature. The solution of azo compound was frozen in acetone-"dry ice" or in liquid nitrogen, evacuated and thawed for degassing. The ampoule was then refrozen, evacuated and sealed. Experiments involving gaseous substances were performed on a Stock-type vacuum apparatus equipped with a standard bulb of calibrated volume of 0.578 liter. The pressure of the vapor in the standard bulb was measured by reading the difference in mercury levels of a monometer 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 at 60 $\pm$ 0.1°C for slightly more than ten half-lives of PAT (4 hours). Ampoules were stored in an acetone-"dry ice" slurry until analyses were performed. Before gas chromatographic analysis each ampoule was broken and a solution of internal standard added to the reaction mixture. The weighed solutions without PAT were checked by GPC for the presence of impurities which would interfere with the determination of the products.

Phenyl radicals will react with oxygen in a competing process with the abstraction reactions as shown by Bridger and Russell (50). The following reaction paths may occur:

$$\phi\cdot + O_2 \xrightarrow{k_O} \phi\text{-}O\text{-}O\cdot \qquad (1)$$

$$\phi\cdot + CCl_4 \xrightarrow{k_C} \phi\text{-}Cl + CCl_3\cdot \qquad (2)$$

$$\phi\cdot + C_6H_{12} \longrightarrow \phi\text{-}H + C_6H_{11}\cdot \qquad (3)$$

In one experiment using $[C_6H_{12}]$ = 4.54M, $[CCl_4]$ = 5.22M and $[PAT]_o$ = 0.1M in an apparatus which shook the mixture continuously under an oxygen atmosphere the results obtained in Table 11 were obtained. The calculation of the k_O/k_C and k_O/k_H values from reactions (1), (2), and (3) above is done in the following manner.

Table 11. Products of the complete decomposition of PAT in cyclohexane and carbon tetrachloride in the presence of oxygen at 60°C

	Total pressure atm.	Oxygen pressure atm.	Chloro-benzene	Benzene	k_O/k_C	k_O/k_H
C_6H_{12}/CCl_4	1.0	0.45	0.27	0.23	630	640

$$[\Delta\phi\cdot] = k_O[O_2][\phi\cdot]$$

$$[C_6H_6] = k_H[C_6H_{12}][\phi\cdot]$$

$$[\phi\text{-}Cl] = k_C[CCl_4][\phi\cdot]$$

$$\frac{k_O}{k_H} = \frac{[\Delta\phi\cdot][C_6H_{12}][\phi\cdot]}{[O_2][\quad\cdot][C_6H_6]} = \frac{[\Delta\phi\cdot][C_6H_{12}]}{[O_2][C_6H_6]}$$

and

$$\frac{k_O}{k_C} = \frac{[\Delta\phi\cdot][CCl_4]}{[O_2][\phi\text{-}Cl]}$$

From Russell and Bridger's work (50)

$$[\Delta \phi\cdot] = 0.74 - ([\phi\text{-H}] + [\phi\text{-Cl}])$$

and the calculations k_O/k_C and k_O/k_H which appear in Table 11 can be made. The k_O/k_C and k_O/k_H results were consistent with those reported by Russell and Bridger (50), that is that phenyl radical reacts more readily with oxygen than do ordinary alkyl or benzylic type radicals

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 (51).

GPC conditions I Two columns were used in series. A 1-meter, 3,3'-oxydipropionitrile (ODPN) column (52), 20% by weight on 80/100 firebrick, was followed by a 1-meter di-n-propyl tetrachlorophthalate column (53), 10% by weight on 80/100 mesh firebrick. Column temperature was 86°C and the helium flow rate was 81 cc/min measured at ambient colditions.

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 112 cc/min.

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

GPC conditions III Two columns were used in series. A 1-meter tris-2-cyanoethoxypropane (TCEP) column, 20% by weight on 80/100 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-propyl tetrachlorophthalate columns were used in series. Temperature was 86°C and helium flow rate was 45 cc/min.

Correction factors Correction factors given in Table 12 conform to the equation:

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

Gas chromotogram areas were measured with an Ott plainimeter. In several reaction mixtures toiling 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 determined by GPC.

Retention times A list of approximate retention times appear in Table 12. With the exceptions of internal standards and the reaction products, no effort was made to determine retention times accurately with very dilute samples. The specificity of all columns decreased after prolonged use. Compounds not eluted in thirty minutes are designated by NE. The order is the same of that in Table 1 with the exception of the first six compounds.

The color of most reaction mixtures as Bridger (14) noted were pale yellow or red. However, in some cases, usually the nitrogen compounds,

Table 12. 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

The reaction mixtures turned dark blue to almost black. These compounds also gave a considerable amount of solid material, but no difficulties were encountered in the analysis.

Table 13. Retention times of various compounds

Compound	GPC conditions	Retention time (min.)
Carbon tetrachloride	I, II, III, IV, V	2.6, 4.2, 3.1,
Benzene	I, II, III, IV, V	5.0, 6.4, 4.6, 7.9, 5.2
Toluene	I, II, III, IV, V	9.2, 12.3, 8.4 13.1, 11.2
Chlorobenzene	I, II, III, IV, V	18.9, 25.6, 16.9 27.4, 22.4
Chlorocyclohexane	I	15.2
sec-Butylbenzene	I	29.5
2-Methylpyrrole	I	N.E.
3-Methylpyrrole	I	N.E.
1,2,5-trimethylpyrrole	IV	N.E.
3-Methylindole	I	N.E.
2-Methylindole	I	N.E.
N-Methylindole	I	N.E.
Indole	III	N.E.
α-Methylnaphthalene	II	N.E.
β-Methylnaphthalene	IV	N.E.
Trimethyl amine	I	0.2
Dimethyl sulfide	I	1.2
Dimethyl disulfide	IV	11.7
Hexamethyl disilane	I	N.E.
Tetraphenyldimethylsilane	III	N.E.

Table 13. (continued)

Compound	GPC conditions	Retention time (min.)
Methyl silicate	IV	22.3
Hexamethylsiloxane	I	1.0
Trimethyl phosphite	I	-
Trimethyl phosphate	I	N.E.
Dimethyl methylphosphonate	V	N.E.
Dimethyl sulfite	IV	N.E.
2,3-Butanedione	I	5.6
Acetophenone	I	N.E.
Methyl benzoate	I	N.E.
Dimethyl carbonate	IV	20.4
Dimethyl peroxide	I	-
Azomethane	I	0.2
Methyl bromide	I	0.8
Methyl iodide	I	1.5
Tetramethylcyclobutane-1,3-dione	IV	N.E.
2,2-Dimethylbenzodioxolane	IV	N.E.
N-Methylphthalimide	IV	N.E.
N,N-Dimethylbenzamide	I	N.E.
Dimethylmercury	I	3.7
Tetramethyltin	II	0.5
β-Methylstyrene	I	N.E.
Methyl thiocyanate	I	N.E.

Table 13. (continued)

Compound	GPC conditions	Retention time (min.)
Ethylmethyl sulfide	I	2.7
Isopropylmethyl sulfide	I	3.5
t-Butylmethyl sulfide	I	N.E.
t-Butylmethyl ether	I	0.7
Di ethyl sulfide	IV	N.E.
Ethylphenyl sulfide	IV	N.E.
Ethylphenyl ether	IV	N.E.
Di ethyl ether	IV	4.4
Ethyl benzoate	I	N.E.
Di ethyl sulfone	IV	N.E.
α-Ethylnaphthalene	I	N.E.
β-Ethylnaphthalene	I	N.E.
Ethyl thiocyanate	I	N.E.
Triethyl amine	IV	3.5
Ethyl bromide	IV	2.5
Propiophenone	IV	N.E.
Di ethylmercury	I	7.2
Isopropyl benzoate	IV	N.E.
Isopropyl bromide	I	16.0
Isopropylphenyl ether	IV	N.E.
Isopropylphenyl sulfide	IV	N.E.
Diisopropyl sulfide	I	N.E.

Table 13. (continued)

Compound	GPC conditions	Retention time (min.)
Diisopropyl disulfide	I	8.5
Diisopropyl ether	I	2.0
Diisopropyl sulfoxide	IV	N.E.
Isopropylphenyl ketone	I	N.E.
t-Butyl alcohol	IV	3.5
Di-t-butyl peroxide	IV	N.E.
t-Butyl chloride	IV	1.5
t-Butyl bromide	IV	1.6
t-Butyl iodide	IV	2.2
Trimethylacetic acid	I	N.E.
t-Butylphenyl sulfide	I	16.6
t-Butylphenyl ether	I	N.E. (85)
t-Butyl benzoate	I	N.E.
Di-t-Butyl disulfide	IV	N.E.
Di-t-Butyl sulfide	IV	25.0
β-t-Butylnaphthalene	IV	N.E.
Dimethoxymethane	IV	5.0
s-Trioxane	IV	16.5
1,4-Pentadiene	I	1.0
Ethylene carbonate	I	6.9
Methylene bromide	IV	8.5
Diphenoxymethane	I	N.E.

Table 13. (continued)

Compound	GPC conditions	Retention time (min.)
Dithiopehnoxymethane	I	N.E.
Malononitrile	IV	N.E.
Ethylene oxide	I	0.4
1,3-Indanedione	IV	N.E.
1,3-Diphenyl-1,3-propanedione	IV	N.E.
3-Pyrroline	IV	20.0
Butadiene sulfone	IV	N.E.
1,4-Thioxane	IV	N.E.
Dioxane	II	15.6
N,N-Dimethyl piperazine	I	2.6
1,3-Dioxolane	IV	20.4
Thioxanthene	I	N.E.
Benzyl alcohol	I	N.E.
Benzyl bromide	I	N.E.
Benzyl chloride	I	N.E.
Phenylacetic acid	I	N.E.
Deoxybenzoin	I	N.E.
N-Benzylphthalimide	I	N.E.
Dimethylbenzyl amine	I	N.E.
1,3-Diphenylacetone	IV	N.E.
Dibenzyl disulfide	IV	N.E.
Acenaphthene	IV	N.E.

Table 13. (continued)

Compound	GPC conditions	Retention time (min.)
Anthrone	IV	N.E.
Xanthene	IV	N.E.
Indene	IV	N.E.
Dibenzyl ether	IV	N.E.
Neopentylbenzene	IV	26.5
Dibenzyl sulfide	IV	N.E.
Benzyl benzoate	IV	N.E.
Bibenzyl	I	N.E.
Oxindole	I	N.E.
Phenylacetonitrile	I	N.E.
Allyl benzene	I	N.E.
Phthalide	I	N.E.
Benzylphenyl ether	IV	N.E.
9,10-Dihydroanthracene	IV	N.E.
Fluorene	IV	N.E.
Benzylphenyl sulfide	IV	N.E.
Dibenzyl sulfoxide	IV	N.E.
1,1-Diphenylethane	IV	N.E.
Diphenylacetonitrile	I	N.E.
Benzal chloride	I	N.E.
Benzal bromide	IV	N.E.
2-Phenyl-1,3-Dioxolane	IV	N.E.

Table 13. (continued)

Compound	GPC conditions	Retention time (min.)
Cyclopentanone	IV	15.4
Tetrahydrofuran	IV	8.0
Thiophene	I	4.0
Tetrahydrothiophene	I	20.0
Pyrrolidene	IV	N.E.
1,1-Dichlorocyclopentane	IV	20.0
Tetramethylene sulfone	I	N.E.
Piperazine	IV	N.E.
Tetrahydropyran	I	6.7
N-Methylmorpholine	I	N.E.
Morpholine	IV	N.E.
Cyclohexanone	I	N.E. (50)
Piperidine	I	N.E. (49)
Pentamethylene sulfide	I	7.9
1,4-Cyclohexadione	IV	N.E.
1,4-Diazabicyclo[2,2,2]octane	I	N.E.
Dimethyl formamide	IV	4.4
Trimethylacetaldehyde	IV	N.E.
Benzaldehyde	IV	N.E.
Methyl formate	IV	N.E.
Tetraphenyldisilane	I	N.E.
Succimide	V	N.E.
Succinic anhydride	III	N.E.

SUMMARY

By the method of competitive reactions, the relative reactivities of a number of functionally substituted compounds toward abstraction reactions by the phenyl radical were determined.

It was found, generally, that the enhancement in reactivity at an α-position due to the functional group is fourfold or less with the consistent exceptions of amino compounds and sulfides. However other apparent abnormalities were also apparent throughout the various types of compounds studied.

Predictions of reactivity in a series of substituted hydrocarbons (substituted alkanes, substituted aralkyl, etc.) based on data obtained in some other series can be made with some overall success but obvious exceptions occur.

Table 14 summarizes the activating or deactivating effect of various substituents when substituted at 1°, 2°, 3°, and benzylic positions.

Table 14. Effect of various substituents when substituted at 1°, 2°, 3° or benzylic positions upon reactivity of the α-carbon-hydrogen bond toward the phenyl radical at 60°C

Substituent (Z)	$(k_{\alpha\text{-H}}/k_{CCl_4})X\ 100$ 1°-Hydrogen $Z\text{-}CH_3$	2°-Hydrogen $Z\text{-}CH_2CH_3$	Z_2CH_2	3°-Hydrogen $Z\text{-}CH(CH_3)_2$	Z_3CH	Benzylic hydrogen $Z\text{-}CH_2C_6H_5$
Alkyl	1.17	7.7	9.1[a]	53.4	47.8[b]	12.6c
Phenyl	8.90	39.3	70	86.3	348	70
Vinyl	12.4	30.0	59	136	--	32.7
Chloro	2.33	--	23.6	--	326	28.0
Bromo	Low	86.4	66	27.1	--	22.15
Iodo	d	d	--	d	--	--
Dimethylamino	33.1	144.4[e]	--	--	--	160.7
Phenylmethylamino	47	--	--	--	--	--
Thiophenyl	12.3	27.15	81	86.8	--	226.4
Thioalkyl	16.8	54	--	106.85	--	--

[a]Hexane used as reference.

[b]3-Methylpentane used as reference.

[c]Neopentylbenzene used as reference

[d]Only iodobenzene formed.

[e]Triethylamine.

Table 14. (continued)

Substituent (Z)	$(k_{\alpha\text{-}H}/k_{CCl_4})X\ 100$ 1°-Hydrogen $Z\text{-}CH_3$	2°-Hydrogen $Z\text{-}CH_2CH_3$	Z_2CH_2	3°-Hydrogen $Z\text{-}CH(CH_3)_2$	Z_3CH	Benzylic hydrogen $Z\text{-}CH_2C_6H_5$
Alkoxy	4.23	32.7	6.85	87.85	--	--
Phenoxy	3.03	13.7	4.5	27.6	--	51.7
Benzoyl	1.11	30.6	7.45	23.0	--	40.05
Acyl	2.93	30.75	14.75	53.0	--	--
Carboxyl	2.8	--	9.0	--	--	27.0
Benzoyloxy	Low	1.5	--	7.02	--	17.0
Cyano	3.0	16.85	65	66.0	--	109.2
Nitro	1.5	7.45	--	17.4	--	--
Alkylsulfinyl	0.63	--	--	6.25	--	35.2
Peroxy	3.01	--	--	--	--	--
Alkyldisulfido	Low[f]	--	--	69.6	--	19.5
α-naphthyl	6.27	22.9	--	--	--	--
β-napthyl	2.35	26.8	--	--	--	--

[f] Displacement also observed.

Table 14. (continued)

Substituent (Z)	$(k_{\alpha\text{-H}}/k_{CCl_4})X\ 100$ 1°-Hydrogen $Z\text{-}CH_3$	2°-Hydrogen $Z\text{-}CH_2CH_3$	Z_2CH_2	3°-Hydrogen $Z\text{-}CH(CH_3)_2$	Z_3CH	Benzylic hydrogen $Z\text{-}CH_2C_6H_5$
Hydroxy	4.43	--	--	--	--	111.1
Benzyl	1.17	--	--	--	--	25.1
Thiocyanato	2.25	11.15	--	--	--	--
Alkylmecuric	6.23	95	--	--	--	--

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