AN ABSTRACT OF THE THESIS OF

Daniel Frank Church for the degree of Doctor of Philosophy

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Title: A STUDY OF THE FREE RADICAL ADDITION OF

THIOPHENOL TO SUBSTITUTED α-METHYLSTYRENES

AND VINYLARENES

Abstract approved:

Dr. Gerald Jay Gleicher

The relative rates of addition of thiophenol to substituted

α-methylstyrenes in benzene at 70°C have been determined. These

relative rates correlated with the Okamoto-Brown sigma-plus sub-

stituent parameters. The rho value thus obtained was -0. 38±0. 02

(correlation coefficient = -0. 984). The relative rates of addition

of substituted thiophenols to p-chloro-α-methylstyrene in benzene

at 70°C also correlated with the sigma-plus parameters to give

a rho value of -0. 27±0. 03 (correlation coefficient = -0. 975). These

results indicate that the transition states of both the addition and

the chain transfer steps for the addition of thiophenol to α-methyl-

styrene involve substantial contributions from charge-separated

forms.

$$\underset{\text{Addition}}{\overset{\displaystyle \overset{CH_3}{\underset{\displaystyle \underset{+\ \cdot\ \ _2\ -}{}}{|}} }{Ph-C-CH_2 : SPh}}$$

$$\underset{\text{Chain Transfer}}{\overset{\displaystyle \overset{CH_3}{|}}{Ph-S \quad H : \underset{\displaystyle \underset{CH_2SPH}{|}}{\overset{\displaystyle }{CPh}}}}$$
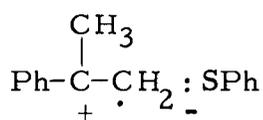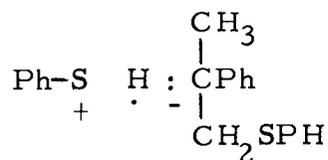
Addition

Chain Transfer

A study was also made of the addition of thiophenol to vinyl-arenes in benzene at 70°C. The relative reactivities determined for this series of compounds were then correlated with various quantities calculated by a semi-empirical SCF-MO method. These calculations utilized a variable bond length approach. The best correlation was between the relative reactivities and the total energy difference between the starting olefin and the intermediate radical. This correlation was better than that obtained using the pi energies alone. Likewise, use of the Hückel method to derive the energy difference or of the free valence led to less satisfactory relation-ships. These results were taken as evidence that the transition state of the addition step has considerable radical character.

Several attempts were also made to find a radical reaction in which the azarene analog of a benzyl-type free radical was generated. The hope was to correlate the relative reactivities for a series of azarene compounds with energy differences calculated similarly to above. However, the nucleophilicity of the nitrogen atom in these systems caused these attempts to be unsuccessful.

A Study of the Free Radical Addition of Thiophenol
to Substituted α-Methylstyrenes
and Vinylarenes

by

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Typed by Opal Grossnicklaus for <u>Daniel Frank Church</u>

To my parents

ACKNOWLEDGEMENTS

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INTRODUCTION

Free Radical Thiol Additions

One of the earliest references to a so-called "abnormal" addition reaction was made by Posner in 1905 (1). For the addition of thiols to olefins, he discovered "that the mercaptan residue was always bound to the carbon with the most hydrogens" (1).

$$RSH + R'CH=CH_2 \longrightarrow R'CH_2CH_2SR \qquad \text{(Eq. 1)}$$

Markownikoff's rule would have predicted just the opposite orientation, the one in which the more negative (mercaptan) residue would be attached to the carbon with the fewest hydrogens (2). In following years, other workers verified Posner's results, and found similar phenomena occurring in other addition reactions, particularly of hydrogen bromide (3-13). A comprehensive, up-to-date review of

$$HBr + RCH=CH_2 \longrightarrow RCH_2CH_2Br \qquad \text{(Eq. 2)}$$
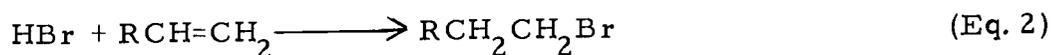
the subject by Mayo and Walling appeared in 1940 (14).

Among the earliest observations associated with this reaction was that the rate of the addition of thiophenol to styrene (Eq. 3) was

$$PhSH + PhCH=CH_2 \xrightarrow{\ h\nu\ } PhCH_2CH_2SPh \qquad \text{(Eq. 3)}$$
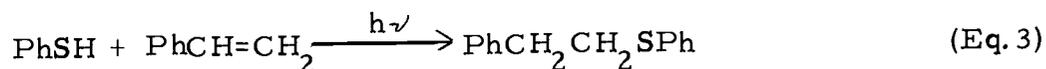
enhanced by light (3). It was soon discovered that peroxides, also, enhanced the rate (4). Such results led Burkhardt to suggest that free radical species might be intermediates in these reactions (5). Finally, Hey and Waters (7) and Kharasch (8, 9) developed this concept into the familiar chain mechanism shown below. The direction

$$X-Y \longrightarrow X\cdot + Y\cdot \qquad (Eq. 4)$$

$$(Eq. 5)$$

$$(Eq. 6)$$
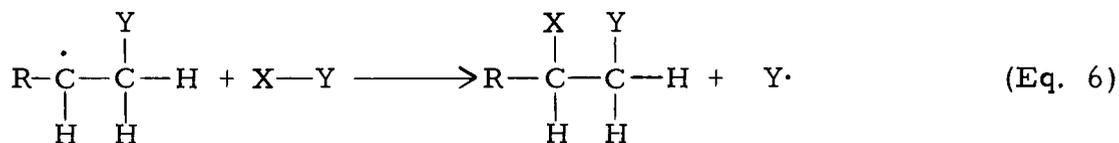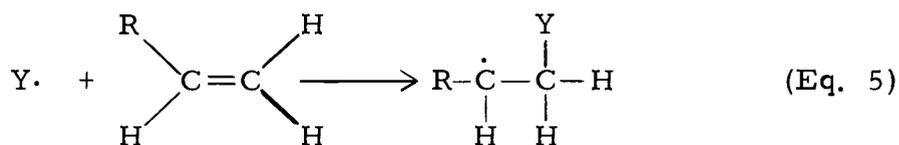
of the addition was attributed to the relative stabilities of the two possible carbon-centered radical intermediates that could be formed in this process (14).

The free radical addition of thiols to olefins is a particularly interesting example of an anti-Markownikoff addition since it is not usually complicated by the competing ionic process and is extremely facile. Sivertz and his coworkers have formulated the complete mechanism as follows (15):

$$\text{Initiation} \qquad RSH \xrightarrow{\ k(I)\ } RS\cdot \qquad (Eq. 7)$$

Attack $\qquad$ RS· + M $\underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}}$ A· $\qquad$ (Eq. 8)

Chain transfer $\quad$ A· + RSH $\xrightarrow{k_{ct}}$ AH + RS· $\qquad$ (Eq. 9)

Propagation $\quad$ A· + M $\xrightarrow{k_p}$ A$_2$· $\qquad$ (Eq. 10)

Termination $\quad$ 2 RS· $\xrightarrow{2k_{t_1}}$ RSSR $\qquad$ (Eq. 11)

$\qquad$ 2 A· $\xrightarrow{2k_{t_2}}$ A$_2$ $\qquad$ (Eq. 12)

$\qquad$ A· + RS· $\xrightarrow{k_{t_{12}}}$ ASR $\qquad$ (Eq. 13)
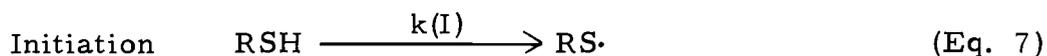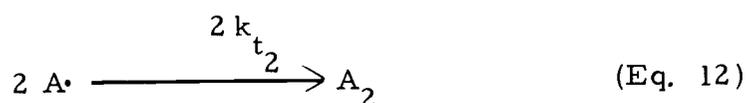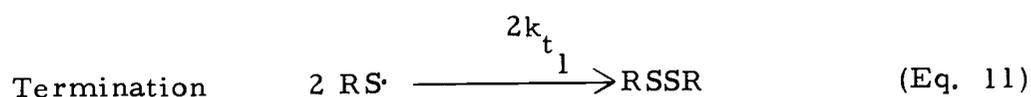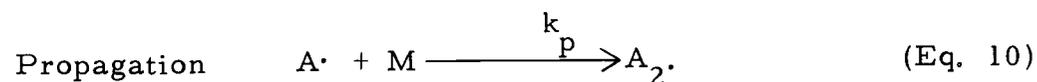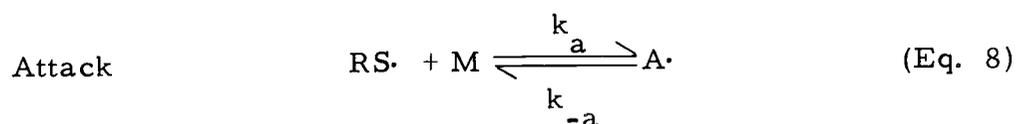
where M is olefin monomer and A· is the adduct radical. Propagation,

in Sivertz' terminology, refers to the telomerization process that

occurs concurrently with the addition.

The reaction may be initiated in several ways. Photolysis,

irradiation with x-rays, γ-rays, or β-rays, or decomposition of

peroxides and azonitriles all have been used to provide the source

of thiyl radicals necessary to start the chain process. Frequently,

even these initiators are not necessary, residual peroxide impurities

in the reagents being sufficient to rupture the weak sulfur-hydrogen

bond (14).

Probably more attention has been paid to the attack step than to any other aspect of this reaction, both with respect to kinetic and stereochemical results. It was demonstrated at an early stage that this addition was often a reversible one. Sivertz et al. showed that in the addition of methyl mercaptan to simple aliphatic olefins, the overall activation energies were negative, an indication that there is a reversible step in the chain process (16). This assertion was conclusively supported by the evidence that thiol-catalyzed cis-trans isomerization of olefins took place more rapidly than chain transfer (17, 18). For example, when the reaction between cis-2-butene

$$
CH_3S\cdot \;+\; \underset{H_3C}{\overset{H}{>}}C=C\underset{CH_3}{\overset{H}{<}} \;\underset{k^c_{-a}}{\overset{k^c_a}{\rightleftharpoons}}\; CH_3S\underset{H}{\overset{}{>}}\underset{CH_3}{\overset{}{C}}\dot{C}\underset{CH_3}{\overset{H}{-}}CH_3
$$

$$\underset{k_{ct}}{\overset{CH_3SH}{\longrightarrow}}$$

$$
CH_3S\cdot \;+\; \underset{H}{\overset{H_3C}{>}}C=C\underset{CH_3}{\overset{H}{<}} \;\underset{k^t_{-a}}{\overset{k^t_a}{\rightleftharpoons}}\; CH_3S\underset{H}{\overset{H_3C}{>}}\underset{CH_3}{\overset{}{C}}\dot{C}\underset{}{\overset{}{-}}H \qquad (Eq.\ 14)
$$
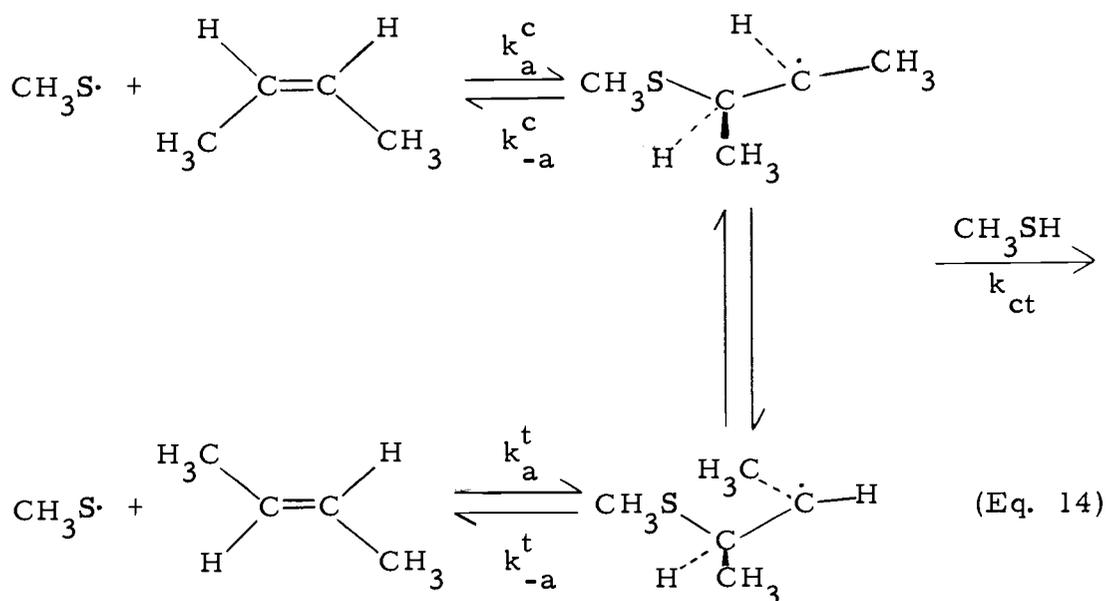
and methyl mercaptan is halted before completion, analysis of the unreacted olefin shows considerable trans-2-butene. In the scheme shown in equation 14, k^c_{-a} and k^t_{-a} are, respectively, 20 and 80 times

greater than k_{ct} (17). These results are in contrast to other radical

additions (e.g., the addition of bromotrichloromethane to 2-butenes)

where no such cis-trans intraconversion is observed (19). That

such reversibility is dependent upon structure, however, can be

seen in the addition of methanethiol to butadiene, a reaction that is

$$CH_3S\cdot + CH_2 = CH - CH = CH_2 \longrightarrow CH_3SCH_2\dot{C}HCH = CH_2 \quad (Eq.\ 15)$$
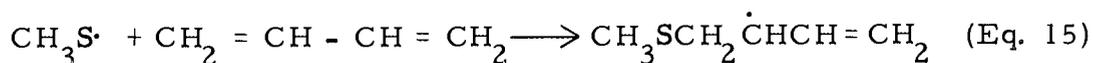
thought to proceed irreversibly via an allylic free radical intermedi-

ate (20). In general, though, the attack step should be regarded as

a low activation energy, reversible one leading to a classical carbon-

centered radical (15, 21-24).

Once formed, the carbon-centered radical can suffer two fates

that will continue the chain. It can abstract a hydrogen atom from

a molecule of thiol (chain transfer) or it can add to a second molecule

of the olefin (propagation). Usually chain transfer is more rapid

than propagation. Thus, in reactions where the thiol concentration

is greater than or equal to that of the olefin, telomerization may

be ignored (25).

In practice, the effects of both the initiation and termination

steps on the overall rate of reaction are minimal. This is due to

the long chain length (about 10^3) of the reaction (15). Thus, the

kinetic treatment can deal with the attack and chain transfer steps

in a straightforward manner. The overall rate expression

formulated by Pallen and Sivertz is (22)

$$\text{Rate of Disappearance} = \frac{[k_{ct}(RSH) + k_p(M)]\,k(I)}{\left[1 + \left(\dfrac{k_t^{RS\cdot}}{k_t^c}\right)^{\frac{1}{2}}\left(\dfrac{k_{ct}(RSH) + k_{-a}}{k_a(M)}\right)\right]k_t} \qquad \text{(Eq. 16)}$$

using the notation in equations 7-12. From this expression, it can
be seen that the rate of olefin disappearance will depend in a first
order manner on both the thiol and the olefin concentrations as long
as the chain transfer is much slower than the attack step and the
attack step and its reverse have comparable rate constants (i. e., the
attack step is approximately thermoneutral).

With the exception of the work dealing with structure-reactivity
relations and their interpretation, this represents the state of the
art as far as the thiol-olefin reaction is concerned up to the early
1960's. Since that time little new work has appeared, although
Griesbaum and Kellog have each submitted recent reviews of the
area (26, 27).

Linear Free Energy Relationships

At this point, a general description of linear free energy rela-
tionships is in order. These are not rigorous thermodynamic deriva-
tions, but rather, are empirical correlations between thermodynamic

quantities of related chemical reactions (28-30). Interpretations

regarding a particular reaction's mechanism, then, depend upon

knowledge of the mechanism of the reaction to which it is compared.

The mathematical development of the relationships between

reaction free energies is quite straightforward. Hammett's treat-

ment involves two basic equations (29)

$$\delta_R \Delta\mu_1^{\ddagger} = a_1 \, \delta_R \, \Delta\mu_1^{\,o} \qquad \text{(Eq. 17)}$$

$$\delta_R \, \Delta\mu_1^{\ddagger} = b_{12} \, \delta_R \, \Delta\mu_{12}^{\ddagger} = a_2 \, b_{12} \, \delta_R \, \Delta\mu_2^{\,o} \qquad \text{(Eq. 18)}$$

where δ_R represents some consistent change that has taken place in

the structures of the reacting molecules 1 and 2, $\Delta\mu^{\,o}$ and $\Delta\mu^{\ddagger}$ are

the free energy changes between the reactant and product or reactant

and transition state, respectively, and a_1, a_2, and b_{12} are propor-

tionality constants. From the relationships between the appropriate

free energy changes and the corresponding reaction rates or equilib-

rium constants, the following equations can then be derived

$$\ln (k/k_o)_2 = A \ln (k/k_o)_1 \qquad \text{(Eq. 19)}$$

$$\ln (K/K_o)_3 = B \ln (k/k_o)_1 \qquad \text{(Eq. 20)}$$

$$\ln (K/K_o)_3 = C \ln (K/K_o)_4 \qquad \text{(Eq. 21)}$$

where each subscript outside the brackets refers to a series of

compounds undergoing the same reaction. Basically, the rates (or

equilibrium constants) of one reaction correspond directly to either

the rates or equilibrium constants of a second, related reaction for

the same variation.

The best known of such linear free energy relationships is

that of Hammett (29)

$$\log k/k_o \text{ (or } \log K/K_o) = \rho \sigma \qquad \text{(Eq. 22)}$$

where sigma is a substituent parameter corresponding to $\log K/K_o$

(K is the acid dissociation constant) for m- and p-substituted benzoic

acids measured relative to the parent compound. The signs and

$$X\text{-}C_6H_4\text{-}CO_2H \underset{}{\overset{K}{\rightleftarrows}} X\text{-}C_6H_4\text{-}CO_2^- + H^+ \qquad \text{(Eq. 23)}$$

$$C_6H_5\text{-}CO_2H \underset{}{\overset{K_o}{\rightleftarrows}} C_6H_5\text{-}CO_2^- + H^+ \qquad \text{(Eq. 24)}$$
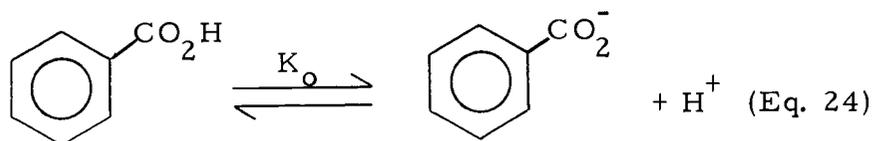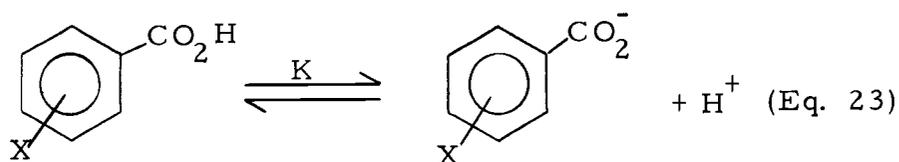
magnitudes of these parameters correlate with the electron withdraw-

ing or donating abilities of the substituents. Negative sigma values

correspond to electron-donating groups, while positive values corres-

pond to electron-withdrawing ones. The magnitude of the reaction

parameter rho is a measure of the relative sensitivity of a particular

reaction to substituent variation and thus, of the polar requirements

of the reaction. The sign of rho reflects the charge character that

develops at the reaction site during a reaction - a negative rho for

reactions involving positive charge and a positive rho for those

involving negative charge.

While the Hammett sigma parameters gave good correlations for

many reactions, for many others they did not. In those situations

where a direct resonance interaction could take place between the

substituent and the reaction site, there was substantial rate enhance-

ment by certain substituents in the _para_ position. Brown and Okamoto

determined a set of sigma-plus parameters based on the solvolysis

of substituted cumyl chlorides (31). The rate enhancement for _para_

substituents is thought to be due to resonance interactions of the type

shown below
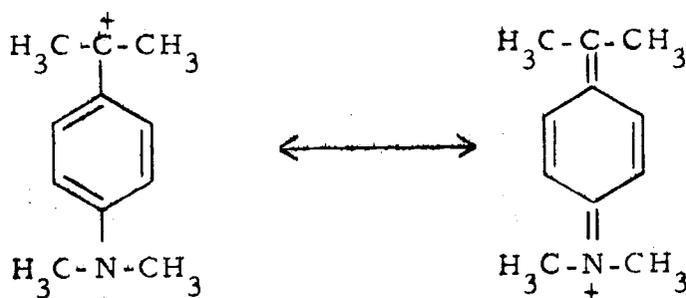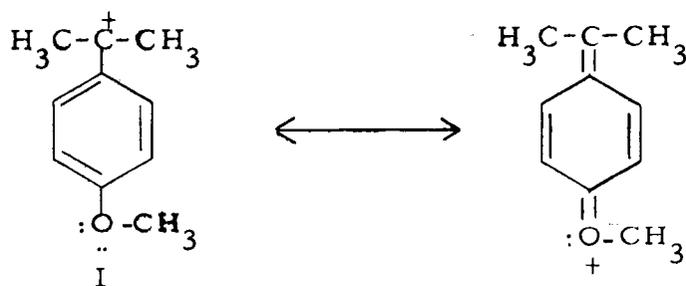
A set of sigma-minus parameters has also been defined for reactions

in which direct resonance interactions can take place between substitu-

ents and a center of negative charge (32). For reactions involving

aliphatic substrates, Taft has developed a similar expression with

the polar parameter sigma-star (33, 34).

Linear free energy treatments have also been successfully

applied to rates of radical reactions. When optimum correlations

have resulted from the utilization of the sigma-plus parameters

(35-40), contributions from forms III and IV to the transition states

for hydrogen abstraction and addition reactions, respectively, have

been postulated (35, 41, 42).

$$[R-\overset{\mid}{\underset{\mid}{C}}-H \cdot X \longleftrightarrow R-\overset{\mid}{\underset{\mid}{C}} \cdot H-X \longleftrightarrow R-\overset{\mid}{C}{}^{+} H \: \ddot{:}X \longleftrightarrow R-\overset{\mid}{\underset{\mid}{C}} \ddot{:} H {}^{+}X]^{\ddagger}$$

III

$$[R-C=\overset{\mid}{\underset{\mid}{C}} \cdot X \longleftrightarrow R-\overset{\cdot}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-X \longleftrightarrow R-\overset{+}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}} \cdot \: \ddot{:}X \longleftrightarrow R-\overset{\cdot\cdot}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}} \cdot \: {}^{+}X]^{\ddagger}$$

IV
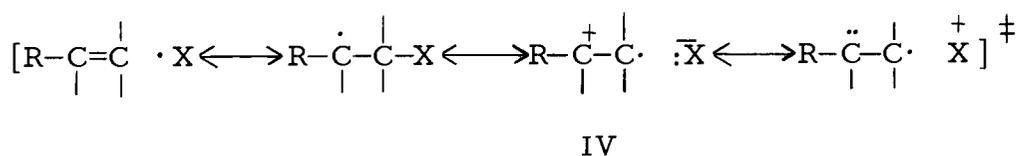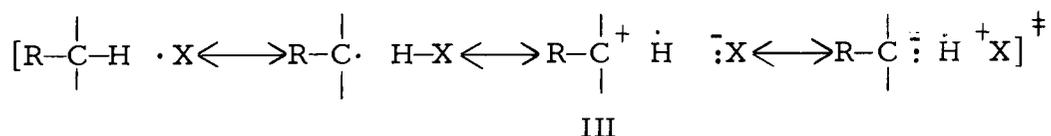
Such forms represent electron transfer preceding atom transfer

and bond formation and are thought to be more important for rela-

tively "unreactive" radicals where the transition state should have

less reactant-like character (36, 43, 44). The similarity of forms

III and IV (R: substituted phenyl) to the transitions state forms I

and II for reactions proceeding through cationic transition states

is apparent.

However, many reactions have also shown better correlations with the sigma parameters (36, 37, 42, 45, 41). This result has led authors to discuss the effects of substituents on reactivity in terms of ground state variations in the electron density at the reaction site or on the bond energy of the reacting bond (40, 46, 48).

There has been some support for the idea that correlations of radical reactivity with either the sigma or the sigma-plus parameters may arise from stabilization of the transition state by resonance and/or polar effects, rather than from the intrinsic properties of the reactants at the reaction site. Several authors have noted that the magnitude of the rho value for radical reactions correlates more closely with the activation energy than with the electron affinity of the attacking radical (36, 37, 49-51).

Early work by Walling et al. (41) yielded results for the reaction between thioglycolic acid and substituted α-methylstyrenes (Eq. 25, R: H) that could be correlated by the sigma-plus substituent

$$HSCH_2CO_2R \; + \; \underset{X}{\text{[ring]}}\overset{\overset{CH_3}{|}}{C}=CH_2 \; \longrightarrow \; \underset{X}{\text{[ring]}}\overset{\overset{CH_3}{|}}{C}HCH_2SCH_2CO_2R \qquad (Eq. \; 25)$$
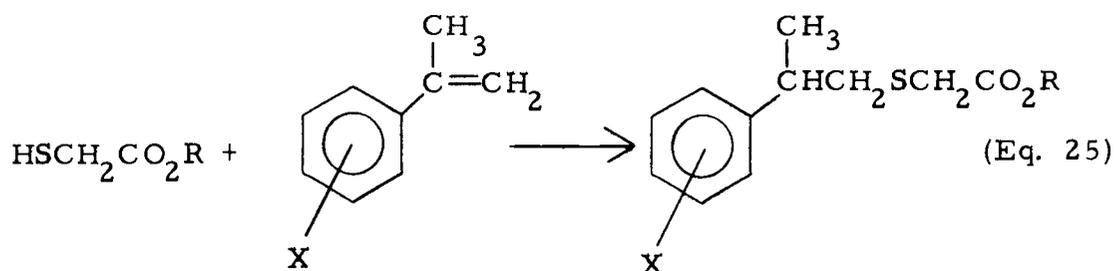
parameters. One curious result of this work was the extraordinarily large reactivity of the olefin when the substituent was the p-methoxy

moiety. This was later shown to be due to the competing acid-catalyzed ionic mechanism (40). This latter study by Cadogan and Sadler also showed good correlations (based on four points) with the sigma-plus parameters for the reactions of methyl thioglycolate with substituted α-methylstyrenes (Eq. 25, R: CH_3) and substituted stilbenes (Eq. 26). These experiments were carried out at $105^{\circ}C$

$$HSCH_2CO_2CH_3 \ + \ \underset{X}{\overset{CH=CHPh}{\bigcirc}} \longrightarrow \underset{X}{\overset{CH_2\overset{\overset{Ph}{|}}{C}HSCH_2CO_2CH_3}{\bigcirc}} \qquad \text{(Eq. 26)}$$
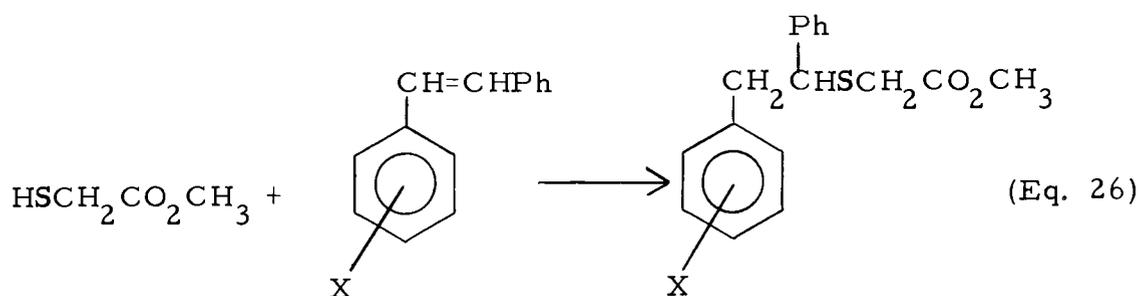
without added solvent. They obtained the same rho value (-0.4) for both reactions. A recent study by Sakai, Miyachi, and Ishii involved a Taft study of the reactions ω-substituted-1-alkenes with alkyl mercaptans (52). Their work further substantiates the polar nature

$$RSH + CH_2 = CH(CH_2)_nX \longrightarrow RSCH_2CH_2(CH_2)_nX \qquad \text{(Eq. 27)}$$

of the transition state, with electron-withdrawing substituents again retarding the reaction.

Molecular Orbital Calculations

There have been two approaches to the correlation of chemical reactivity with calculated quantities. These are the use of ground

state properties like charge density, bond order, free valence, self-polarizability, frontier electron density, and superdelocalizability (53) or the use of calculated energy differences to approximate the energy change between the reactant and transition states (54). One viewpoint is that as the reaction becomes more exothermic and the transition state more closely resembles the reactants (44), that the intrinsic properties of the reactant molecules themselves will affect their reactivity (53). In contrast is the assertion of Dewar and Thompson (54) that when dealing with reaction rates or equilibria (quantities related to free energy changes), correlation with calculated energy differences should be expected while correlations with ground state parameters would be fortuitous.

An inherent problem in dealing with the transition state is that its energy can not be calculated (54, 55). However, this may not be a serious problem. Evans and Polanyi have observed that there is often a linear relationship between the free energy of activation and the free energy of the reaction (56). Utilizing the

$$\Delta G^{\ddagger} = a + b \Delta G \qquad \text{(Eq. 28)}$$

relation between free energy and the rate constant, this equation can be rewritten as

$$-RT \log k = a' + b' \Delta G \qquad \text{(Eq. 29)}$$

i. e., there is a linear corresponcence between the log of the rate

of a reaction and its free energy. Assuming, then, that the entropy

change is constant for a series of closely related reactions, equation

30 follows

$$-RT \log k = A + c \Delta H \qquad \text{(Eq. 30)}$$

Now, the enthalpy of a reaction is a quantity that can be calculated

by molecular orbital theory, it being the difference in the calculated

energies of the product and reactant states. Further, the constant c

could be regarded as a measure of the transition state character,

since smaller c corresponds to a more exothermic reaction. This

is the same as saying that a lower value of c implies a transition

state that more closely resembles the reactants (44). The important

point, according to Dewar, is that there should always be a correla-

tion of reaction rates and calculated energy differences (43).

There have been a number of studies in which chemical reac-

tivity and energy differences calculated by molecular orbital methods

have been correlated. Some of the systems for which such treatments

have been successful involve arylmethylcarbanions (54, 57, 58),

arylmethylcarbonium ions (51, 59-63), and arylmethyl radicals (64,

65). Electrophilic and radical aromatic substitutions have been

correlated by similar methods (54).

In order to calculate the energies involved in such treatments,

it is generally useful to invoke the so-called Hückel approximation

(66). This treatment assumes that the total energy of a compound may be broken up into components ascribed to the sigma- and pi-bonds.

$$E_{Total} = E_\sigma + E_\pi \qquad \text{(Eq. 31)}$$

What is calculated from molecular orbital theory is the pi-energy, while the sigma-energy component can be calculated using localized-bond models.

Of the several treatments available for determining the pi-electron energy of hydrocarbons, the one described by Pople has found extensive utility (67, 68). The energy calculated is that of n pi-electrons in a field set up by a core of n atoms carrying a total charge of +n. The method of Roothan is used (69), with the elements of the F-matrix being given by

$$F_{ii} = W_i^c + \tfrac{1}{2} q_i \, (ii, ii) + \sum_{\substack{j \\ j \neq i}}^{j} (q_i - 1)(ii, jj) \qquad \text{(Eq. 32)}$$

$$F_{ij} = \beta_{ij}^c - \tfrac{1}{2} p_{ij} \, (ii, jj) \qquad \text{(Eq. 33)}$$

where W_i^c is the valence state ionization potential for an electron in a carbon 2p-orbital, (ii, ii) represents the repulsion between two electrons centered on atom i, (ii, jj) represents the repulsion between an electron on atom i and one on atom j. β_{ij}^c is the core resonance integral for an electron in an orbital between i and j, q_i and q_j are

charge densities, and p_{ij} is the bond order for the bond between ι

and j. The use of these equations for calculations is fairly simple

once the integrals have been determined. The approach developed

by Dewar and his coworkers has been to derive these integrals utiliz-

ing appropriate semi-empirical parameters, the values of the param-

eters being adjusted to give suitable fits to experimental data. The

technique has been applied to closed-shell hydrocarbons (70-72)

and heteroatom compounds (73, 74), as well as to open-shell radical

sytems (75).

DISCUSSION OF THE PROBLEM

This work can be divided into two separate aspects of the same problem. The first involves a Hammett-type study (29) of the addition of thiophenol to α-methylstyrene. The second part incorporates a correlation between semiempirical SCF-MO calculations of energy differences and the reactivities of vinylarenes towards the same thiol moiety.

The reaction chosen for the first part of this study was that between thiophenol and α-methylstyrenes. There are several

PhSH + (Eq. 34)
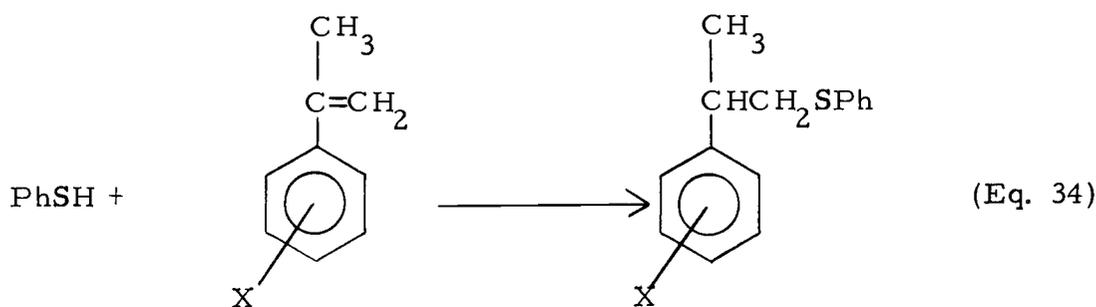
factors bearing on the choice of this system. The kinetics of thiol additions to olefins have been worked out by Sivertz and his coworkers (15, 20-22), and it has been shown that in the case of styrene reacting with thiophenol the rate-determining step is the chain transfer (Eq. 37), the rate being dependent on olefin concentration only at

$$PhSH + PhCH{=}CH_2 \longrightarrow PhCH_2CH_2SPh \qquad (Eq.\ 35)$$

$$PhS\cdot\ + PhCH{=}CH_2 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} Ph\overset{\cdot}{C}HCH_2SPh \qquad (Eq.\ 36)$$

$$\overset{\cdot}{\text{Ph}}\text{CHCH}_2\text{SPh} + \text{PhSH} \xrightarrow[\text{r. d. s.}]{k_{ct}} \text{PhCH}_2\text{CH}_2\text{SPh} + \text{PhS}^{\cdot} \qquad (\text{Eq. 37})$$
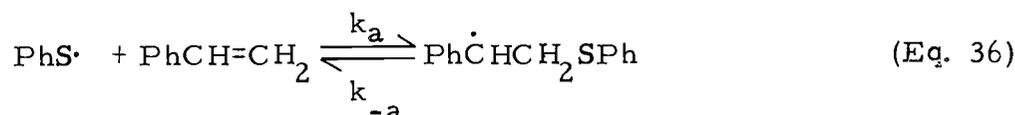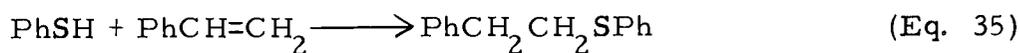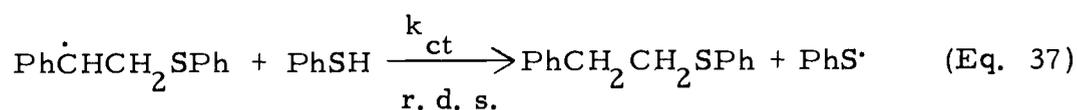
low values (22). As seen earlier, this sort of kinetic dependence

reflects an initial attack step that is readily reversible. Thus, it

should be interesting to compare the dependence of this facile addi-

tion step on substituents in the α-methylstyrene moiety with the well-

documented dependence shown in radical hydrogen abstractions (35-

37, 39, 42, 47, 50) and non-reversible radical additions (38).

The general result obtained for hydrogen abstractions by

electrophilic attacking radicals is enhancement by electron-donating

groups. It also appears that the more stable the intermediate radical,

the lower the absolute value of rho. Prior to this work, only one

extensive Hammett-type treatment of a radical addition to styrene -

that of Sakurai et al. for the addition of trichloromethyl radical

$$\cdot\text{CCl}_3 + \underset{\text{X}}{\overset{\text{CH=CH}_2}{\bigcirc}} \longrightarrow \underset{\text{X}}{\overset{\overset{\cdot}{\text{C}}\text{HCH}_2\text{CCl}_3}{\bigcirc}} \qquad (\text{Eq. 38})$$
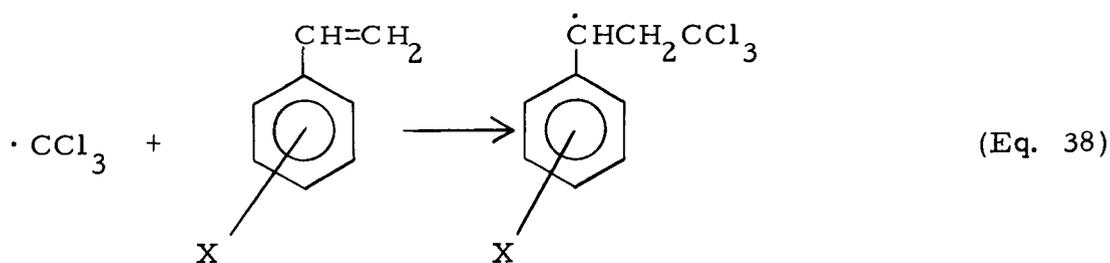
had been reported (38). The rho value they obtained by a correlation

with the sigma-plus parameters was -0.42. The authors proceeded

to modify these results by introducing extra delocalization effects

into the substituent parameters for all para groups irrespective of

electronic character (76). For related thiol additions, the Taft

treatment of alkyl mercaptan addition to ω-substituted-1-alkenes by

Sakai et al. showed that inductively electron-withdrawing substituents

retarded the reaction (52). For substituted styrenes, Walling et al.

have qualitatively shown the same result (41), while Cadogan and

Sadler have attempted a quantitative treatment utilizing just four

points (40). Thus, it appears that the addition step in reactions may

show a structure-rate relationship similar to those observed in more

selective hydrogen abstractions. It was felt that it would be useful

to confirm this fact as the initial study.

Substituent effects on the chain transfer step could also be

studied. It was decided to allow p-chloro-α-methylstyrene to react

competitively with substituted thiophenols. This choice of olefin is

(Eq. 39)
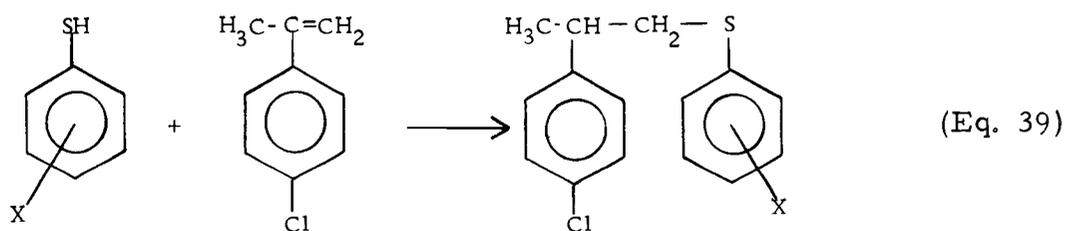
an arbitrary one, although it was made with consideration for the

ease of experimental analysis. Comparison to the work of Kooyman

et al. on hydrogen abstraction from substituted thiophenols by

(Eq. 40)
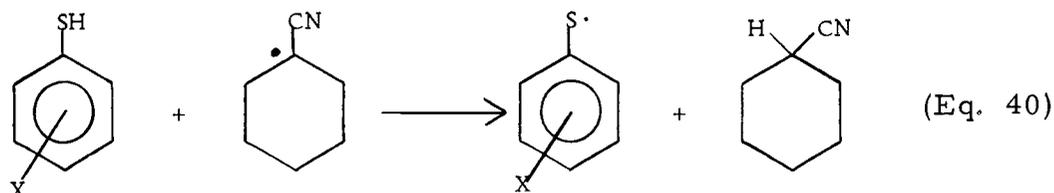
1-cyano-1-cyclohexyl radicals should be interesting (77). They

obtained a rho value of -0.53 by correlation with the Hammett sigma

constants.

The second aspect of this work is the extension of the work of

Gleicher and Unruh (65). That study involved the correlation of the

rates of hydrogen abstraction from methylarenes by either trichloro-

methyl or tert-butoxy radicals with the calculated pi-energy difference

$$\text{ArCH}_3 + \begin{cases} \cdot\text{CCl}_3 \\ \underline{t}\text{-BuO}\cdot \end{cases} \longrightarrow \text{Ar}\overset{\cdot}{\text{C}}\text{H}_2 + \begin{cases} \text{HCCl}_3 \\ \underline{t}\text{-BuOH} \end{cases} \qquad (\text{Eq. 41})$$
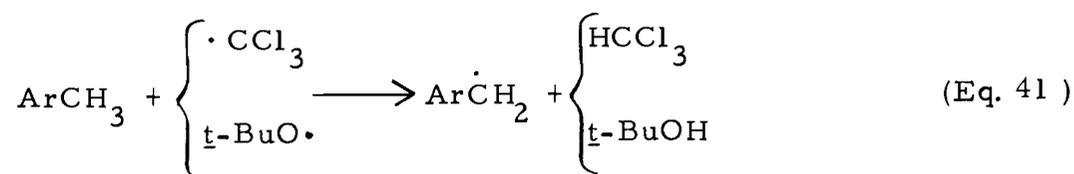
between the starting material and the corresponding radical. These

calculations were carried out using a semi-empirical, self-consistent

field molecular orbital approach. They found an excellent correla-

tion for the reaction with trichloromethyl radical, but a poor one

for that involving tert-butoxy radical. Since the reaction with the

latter radical was considerably more exothermic than with the

former, it was felt that the transition state for the reaction involving

$$[\text{ArCH}_2\text{--H}\cdot\text{X}\longleftrightarrow\text{Ar}\overset{\cdot}{\text{C}}\text{H}_2\text{H--X}\longleftrightarrow\text{Ar}\overset{+}{\text{C}}\text{H}_2 \quad \overset{\cdot}{\text{H}} :\overset{..}{\text{X}}\longleftrightarrow\text{Ar}\overset{..}{\text{C}}\text{H}_2 \quad \overset{\cdot}{\text{H}} \overset{+}{\text{X}}]$$

$$\text{V} \qquad\qquad \text{VI} \qquad\qquad \text{VII} \qquad\qquad \text{VIII}$$
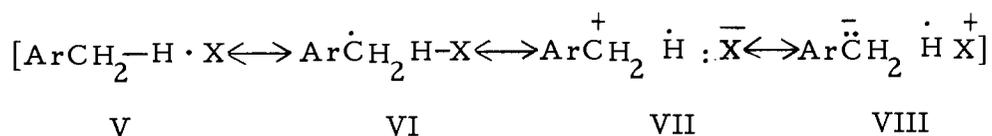
the tert-butoxy radical might be best represented by assuming a

strong contribution from the reactant-like form V. Thus, ground

state parameters calculated for the methylarene reactants were

used in correlations with the experimental reactivities. However, these correlations were also poor.

It was felt that the addition of thiophenol to vinylarenes might provide an interesting example to further test this technique. The addition process differs from the abstractions previously studied in that the radical-generating step is very much more facile. It is not, in fact, the rate-determining step, and it is probably reversible.

Improvements over the former study can also be made. Improved computer facilities allow the use of a variable bond length calculation wherein a new set of bond lengths is calculated _via_ a linear bond order-bond length relation at the end of each iteration. These new bond lengths are then used to calculate new values of the repulsion and resonance integrals in the following iteration (72, 74). A greater degree of self-consistency should be reached. The sigma-energy will also vary from bond to bond and the total energy, being the sum of the sigma- and pi-energies, may more closely reflect the bond length variation observed in "real" molecules. Extension to heteroatomic systems is also possible. Such systems have been studied by this SCF-MO treatment and the calculated heats of atomization have shown close correlation with experimental values (74, 78).

It was originally planned to investigate isopropenylarenes. These are analogous to the α-methylstyrenes of our first study.

During the course of these studies, however, it was decided to switch from the isopropenylarene system to the vinylarenes. This change would certainly not be expected to modify any of the comments based on the results from the former system. Relative rates would then be determined for thiophenol reacting with pairs of vinylarenes, as well as for vinylheteroarenes.

RESULTS

Synthesis of Substituted α-Methylstyrenes

Two approaches were followed in the preparation of the substituted α-methylstyrenes. For most compounds, the addition of a Grignard reagent to a carbonyl compound gave the appropriately substituted cumyl alcohol, which was then dehydrated (Scheme I).

Scheme I
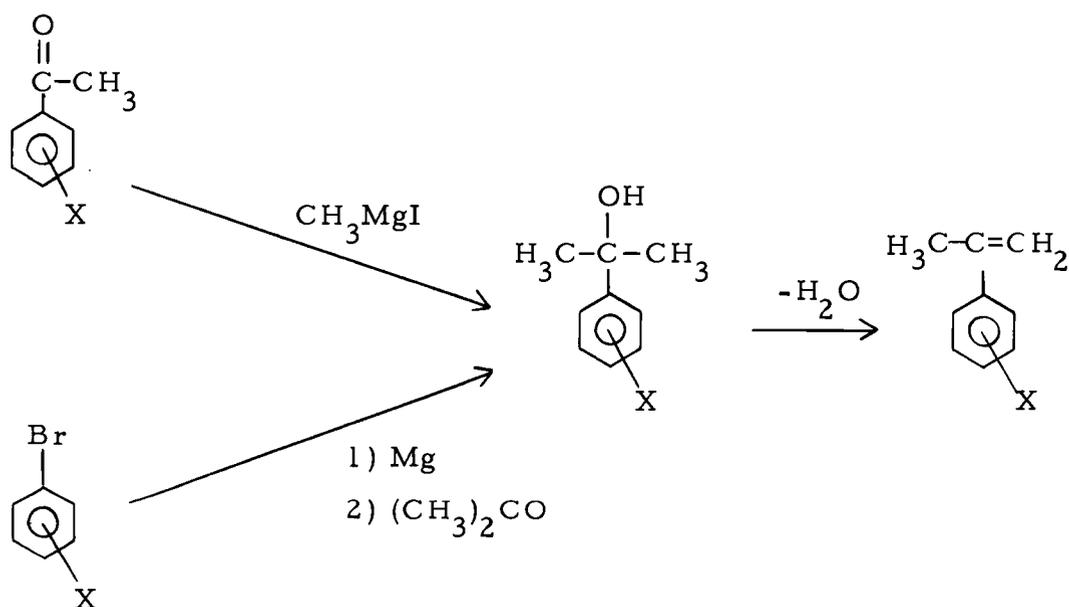
In the synthesis of p-nitro-α-methylstyrene, Scheme II was followed.
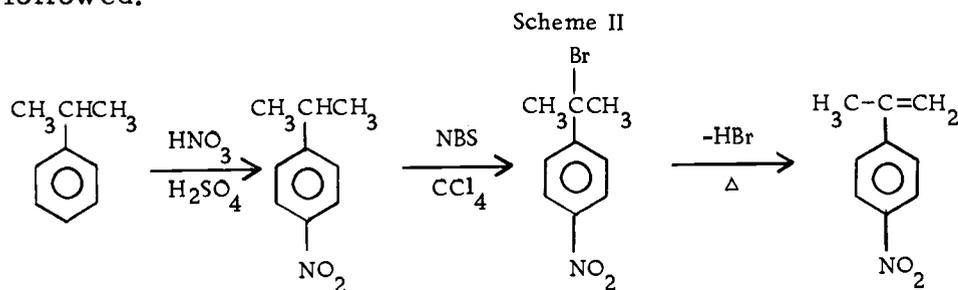
Scheme II

Synthesis of Isopropenylarenes

The procedure for the synthesis of the isopropenylarenes was

essentially the same as above - organometallic addition to a carbonyl

followed by dehydration of the resulting 2-arylpropan-2-ol (Scheme

III). One of the problems encountered with this procedure was that

Scheme III

$$
\underset{\text{Ar-C-CH}_3}{\overset{\overset{\text{O}}{\|}}{}}
$$

CH$_3$MgI

Ar-Br

1) Mg or Li

2) (CH$_3$)$_2$CO

$$
\underset{\overset{|}{\text{CH}_3}}{\overset{\overset{\text{CH}_3}{|}}{\text{ArC-OH}}} \xrightarrow{-\text{H}_2\text{O}} \underset{}{\overset{\overset{\text{CH}_3}{|}}{\text{Ar-C=CH}_2}}
$$

CH$_3$MgI

ArCO$_2$R
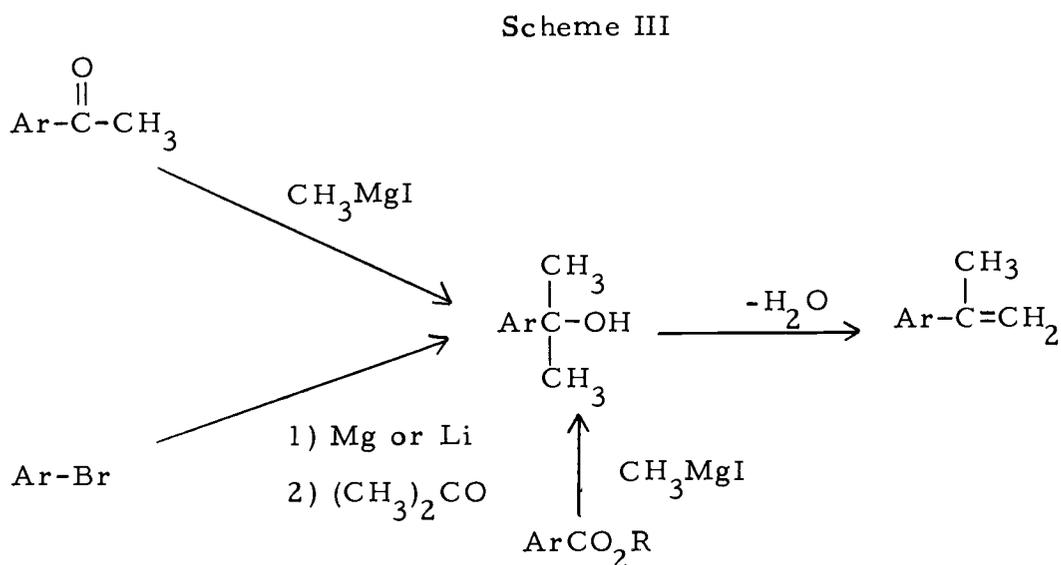
the final dehydration step was frequently accompanied by large

amounts of polymerization.

Another scheme (IV) was also tried - a Wittig reaction of an

appropriate acetyl compound with methylene ylid. This procedure

Scheme IV

$$
\underset{\text{Ar-C-CH}_3}{\overset{\overset{\text{O}}{\|}}{}} \xrightarrow{\overset{-}{\text{CH}_2}\text{-}\overset{+}{\text{P}\phi_3}} \underset{}{\overset{\overset{\text{CH}_3}{|}}{\text{Ar-C=CH}_2}}
$$
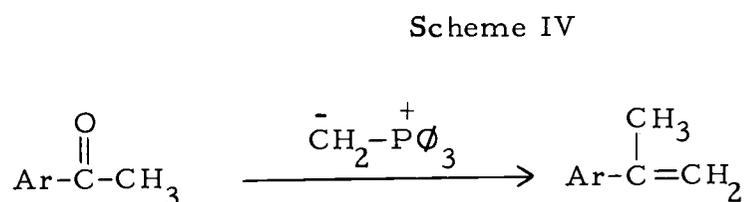
seemed to generally suffer from poor reactivity resulting in mixtures

of starting ketone and olefin product that were difficult to separate.

Synthesis of Vinylarenes

As noted above, polymerization during the final elimination

step is a problem in synthesizing reactive olefins _via_ alcohol inter-

mediates. Therefore, an alternative procedure involving the Wittig

reaction was employed (Scheme V).

Scheme V

$$Ar-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{KOCl} Ar-CO_2H \xrightarrow{CH_3OH, H^+} Ar-CO_2CH_3$$

$$\begin{array}{c} \text{1) Mg or Li} \\ \text{2) CO}_2 \end{array} \qquad \xrightarrow{\text{LiAlH}_4} \qquad \text{LiAlH}_4$$

$$Ar-Br \xrightarrow[\text{2)HCHO}]{\text{1) Mg}} Ar-CH_2OH$$

$$\qquad\qquad\qquad\qquad PBr_3$$

$$Ar-CH=CH_2 \xleftarrow[\text{2) HCHO}]{\text{1) } \emptyset \text{ Li}} Ar-CH_2\overset{+}{P}\emptyset_3\overset{-}{Br} \xleftarrow{P\emptyset_3} Ar-CH_2Br$$
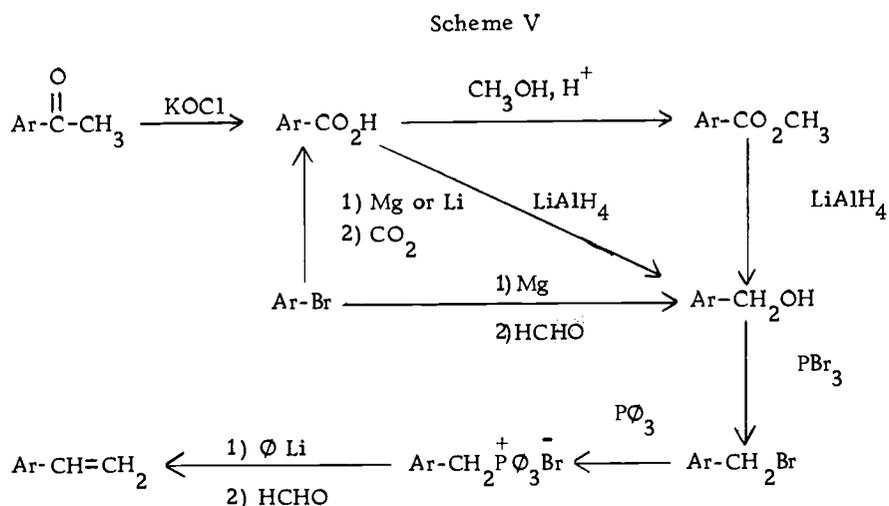
There were two reasons for choosing to make the Wittig reagent

using the "aromatic half" of the double bond. The first was a matter

of reactivity. As seen earlier, reacting methylene ylid with a large

molecular weight carbonyl compound does not always proceed cleanly

to give reasonable yields of olefin. Also, if methylene ylid were

used, it would be necessary to prepare aldehyde derivatives of the

polycyclic compounds. The synthesis of these compounds is not read-

ily accomplished. For these reasons, the particular sequence of

relatively simple reactions was developed.

Reaction of Thiophenol and α-Methylstyrene

Photolysis of a refluxing solution of α-methylstyrene, thiophenol, and benzene gave only one product in 93.6% yield. The nmr spectrum of this product is that expected for the anti-Markownikoff adduct, β-thiophenoxyethylbenzene.

Reaction of Thiophenol and p-Methoxy-α-methylstyrene

Similar photolysis of p-methoxy-α-methylstyrene and thiophenol in refluxing benzene also gave only one product as determined by nmr. The spectrum is consistent with that of β-(p-methoxythiophenoxy)ethylbenzene.

In view of the stability of the intermediate radical derived from p-methoxy-α-methylstyrene, it might be expected that this compound is prone to polymerization. To investigate this possibility, the olefin and thiophenol were reacted in benzene at 70.0°C (photoinitiation). Analysis by glc showed that less than 5% of the olefin might be disappearing via polymerization.

Reaction of Thiophenol and p-Nitro-α-methylstyrene

To estimate the extent to which p-nitro-α-methylstyrene might undergo polymerization, that olefin and a small amount of thiophenol were photolyzed in benzene in 70.0°C. The thiophenol disappeared

completely. More than twice the expected amount of p-nitro-α-methylstyrene disappeared.

Overall Reversibility of Addition of Thiophenol to α-Methylstyrene

$$H_3C-C=CH_2 \text{ (Ar=p-OCH_3 phenyl)} + PhCHCH_2SPh \xrightarrow{?} H_3C-CHCH_2SPh \text{ (Ar=p-OCH_3 phenyl)} + Ph-C=CH_2$$

(Eq. 42)
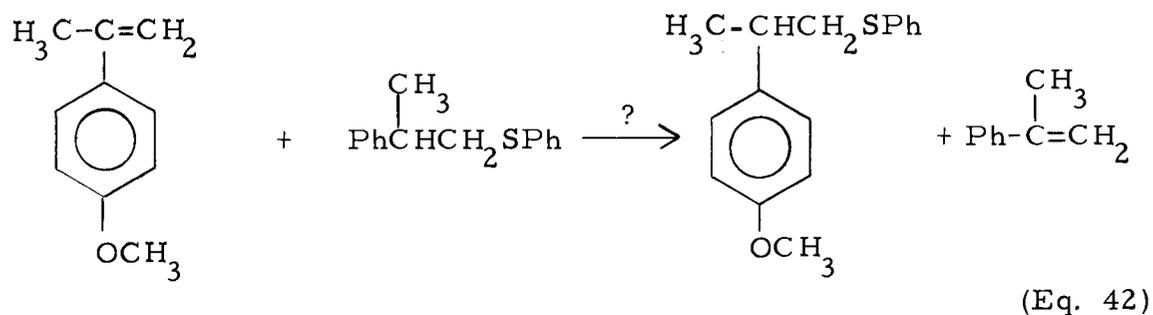
To determine whether both steps in the chain process might be reversible, equimolar amounts of p-methoxy-α-methylstyrene and β-thiophenoxyethylbenzene were photolyzed in benzene at 70.0°C. After a period comparable to a typical kinetics experiment, glc analysis indicated essentially no decrease in the concentration of either species.

Reaction of Thiophenol and 1-Vinylnaphthalene

Photolysis of a benzene solution of 1-vinylnaphthalene and thiophenol at 70.0° C gave rise to one product that had an nmr spectrum consistent with that of the expected sulfide.

28

Catalysis of the Reaction between Thiophenol and
p-Methoxy-α-methylstyrene by Pyridine

In order to determine whether the basicity of pyridine compli-
cated the addition of thiophenol to vinylarenes, two solutions were
prepared, each having similar concentrations of thiophenol and
p-methoxy-α-methylstyrene, as well as an internal standard for glc
analysis. One of these solutions also contained an equivalent amount
of pyridine. The results indicate an enhancement of the rate of
disappearance of the olefin in the presence of the added pyridine.

Reaction of Pyridine and Bromotrichloromethane

Pyridine and bromotrichloromethane were refluxed together.
The solution took on an orange color and a black solid precipitated out
of the solution. The nmr spectrum of this water soluble solid sug-
gested that a reaction at the pyridine nitrogen had occurred.

Reaction of Pyridine and N-Bromosuccinimide

Equimolar amounts of pyridine and N-bromosuccinimide to-
gether with 1% of benzoyl peroxide as an initiator, were refluxed in
carbon tetrachloride. Again, the solution became red-orange in
color and a black substance coated the succinimide. Analysis showed
that the pyridine had disappeared.

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color and a black substance coated the succinimide. Analysis showed
that the pyridine had disappeared.

Relative Reactivities of Substituted α-Methylstyrenes
towards Thiophenol

The relative reactivities of substituted α-methylstyrenes towards the thiyl radical derived from thiophenol in benzene at $70.0^{\circ}C$ have been determined in competitive experiments by direct analysis of the disappearance of the two olefins (Table 1). The resulting rho values for the correlations with the sigma and sigma-plus parameters, together with the correlation coefficients are listed in Table 2. The reactivity of p-nitro-α-methylstyrene clearly seemed to be anomalous and was, therefore, omitted in all correlations. Figure 1 depicts the correlation between the reactivities and the sigma-plus substituent parameters.

Relative Reactivities of Substituted Thiophenols
towards p-Chloro-α-methylstyrene

To investigate direct changes upon the chain transfer step, pairs of substituted thiophenols were reacted with p-chloro-α-methylstyrene in benzene at $70.0^{\circ}C$. The results obtained by direct comparisons of the disappearances of the two thiophenols are listed in Table 3, while the calculated rho values are shown in Table 4. Figure 3 graphically shows the best correlation.

Table 1. Relative reactivities of substituted α-methylstyrenes towards thiophenol at 70. 0°C

Substituent	k_X/k_H[a]	k_X/k_H[b]	σ[c]	σ^+[c]
p-CH$_3$O	1. 85±0. 13[d]	1. 13±0. 15[d]	-0. 27	-0. 778
p-CH$_3$	1. 36±0. 18	1. 23±0. 29	-0. 17	-0. 311
m-CH$_3$	1. 15±0. 09	0. 88±0. 20	-0. 07	-0. 066
H	1. 00	1. 00	0	0
m-CH$_3$O	1. 02±0. 07	0. 61±0. 13	0. 12	0. 047
p-Cl	0. 98±0. 04	0. 74±0. 07	0. 23	0. 114
m-Cl	0. 69±0. 10	0. 42±0. 11	0. 37	0. 399
m-CF$_3$	0. 58±0. 07	0. 50±0. 09	0. 47	0. 52
p-NO$_2$	0. 99±0. 10	0. 57±0. 11	0. 78	0. 790

a) By direct comparison method   c) Reference 27

b) By indirect comparison method   d) Average deviation

Table 2. Reaction constants for the addition of thiophenol to substituted α-methylstyrenes[a]

Substituent Parameter	Reaction Constant Direct method of analysis	Correlation Coefficient
σ	-0. 57±0. 03[b]	-0. 962
σ^+	-0. 38±0. 02	-0. 984

a) The point corresponding to the p-nitro compound has been omitted from all of these correlations
b) Average deviation
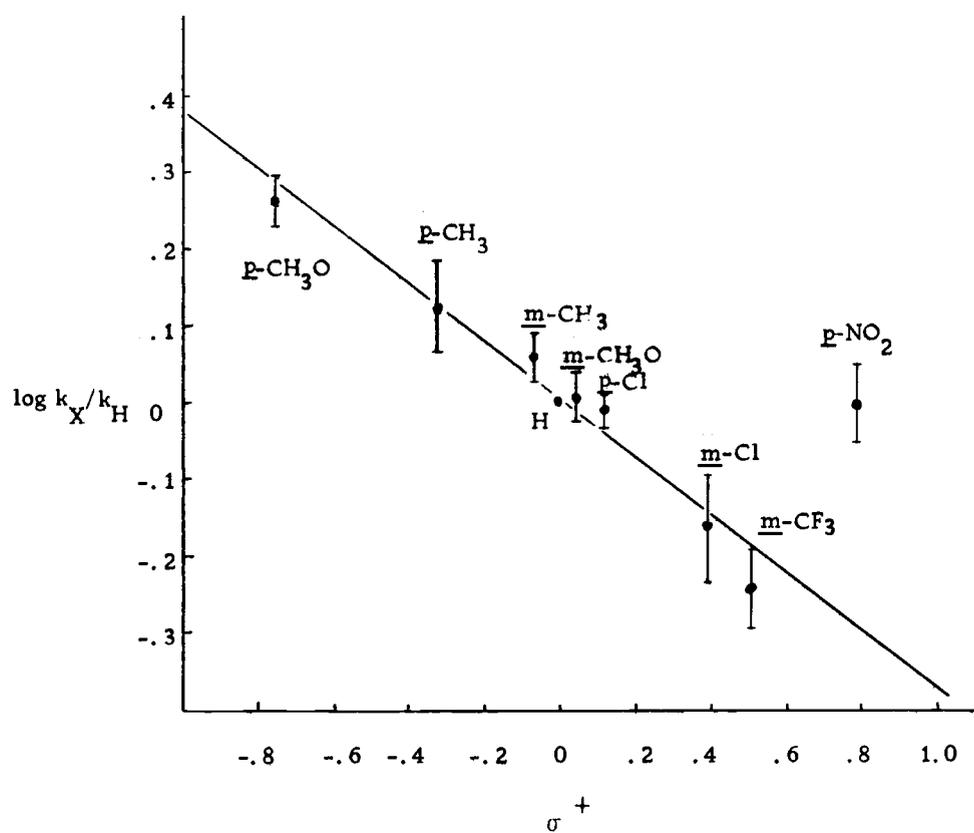
Figure 1. Correlation of log k_X/k_H and σ^+ for the reaction of substituted α-methylstyrenes and thiophenol. Direct method of analysis.
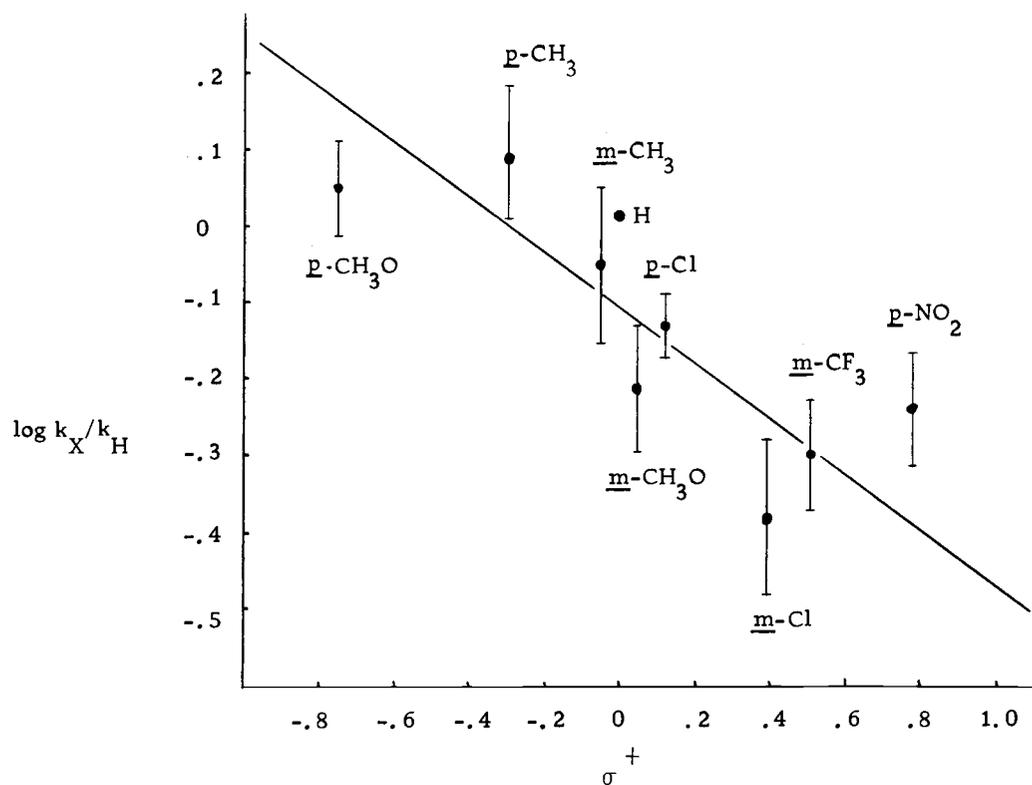
Figure 2.   Correlation of log k_X/k_H and σ^+ for the reaction of substituted α-methylstyrenes and thiophenol.   Indirect method of analysis.

Table 3. Relative reactivities of substituted thiophenols towards β-thiophenoxy-p-chlorocumyl radicals at 70.0°C.

Substituent	k_X/k_H	σ [a]	σ^+ [a]
p-CH$_3$O	1.65±0.09[b]	-0.27	-0.778
p-CH$_3$	1.00±0.02	-0.17	-0.311
H	1.00	0	0
p-Cl	0.87±0.08	0.23	0.114
p-NO$_2$	0.54±0.06	0.78	0.790

a) Reference 27

b) Average deviation

Table 4. Reaction constants for the addition of substituted thiophenols and p-chloro-α-methylstyrene.

Substituent Parameter	Reaction Constant	Correlation Coeff.
σ	-0.35±0.05[a]	-0.910
σ^+	-0.27±0.03	-0.975

a) Average deviation
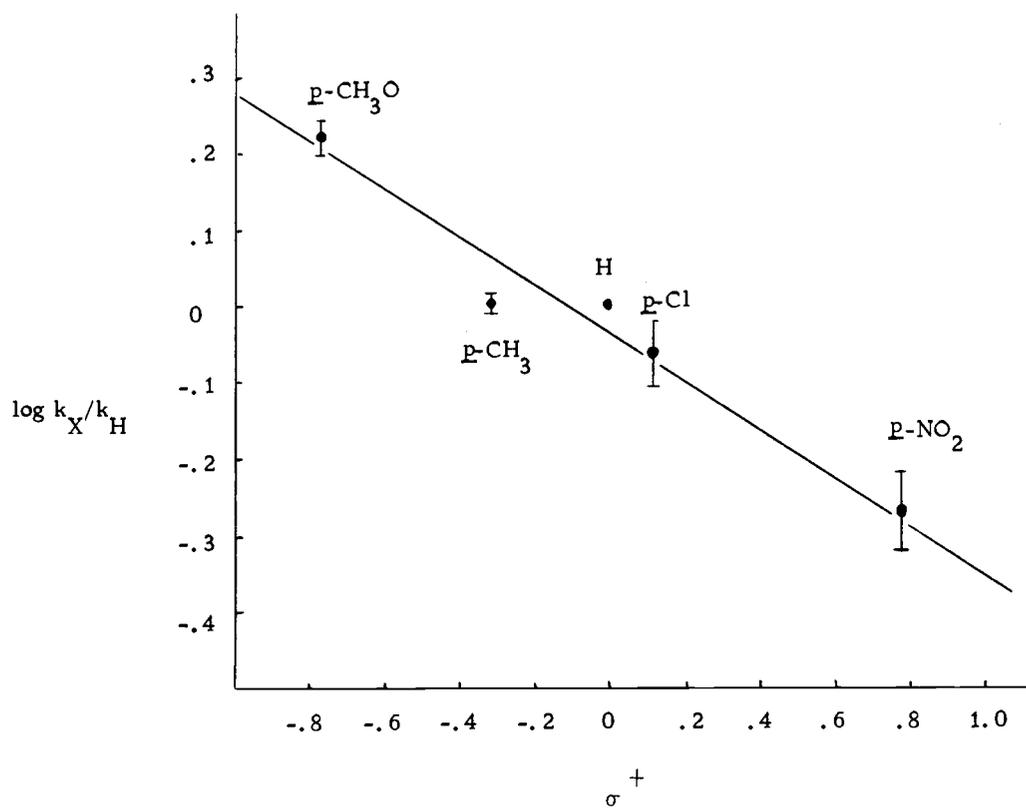
Figure 3. Correlation of log k_X/k_H and σ^+ for the reaction of
substituted thiophenols and p-chloro-α-methylstyrene.

<u>Relative Reactivities of Isopropenylarenes</u>
<u>towards Thiophenol</u>

The relative reactivities of isopropenylarenes towards the thiyl

radical derived from thiophenol in benzene were determined at 70.0°C

by the disappearance of the two competing olefins. The results, to-

gether with the corresponding changes in the total binding energy are

presented in Table 5.

Table 5. Relative reactivities of isopropenylarenes towards
thiophenol at 70°C.

Compound (Fig. 4 R: $C(CH_3)=CH_2$)		k_X/k_{std}	$\Delta\Delta_{Total}$ (e. v.)[a]
Phenyl	(IX)	0.65 ±0.07[b]	0
1-Naph.	(X)	0.095±0.01	0.170
2-Naph.	(XI)	1.00	0.056
9-Anth.	(XIV)	0.015±0.005	0.507
9-Phenanth.	(XV)	0.033±0.005	0.173

a) Energy change relative to α-methylstyrene

b) Average deviation

<u>Relative Reactivities of Vinylarenes</u>
<u>towards Thiophenol</u>

Benzene solutions of thiophenol, a vinylarene, and p-methoxy-

α-methylstyrene (reference olefin) were reacted at 70.0°C. Initiation

was by either direct photolysis (styrene, naphthalene, phenanthrene, and

chrysene derivatives) or by benzoyl peroxide decomposition (anthracene

IX   X   XI

XII   XIII   XIV

XV   XVI   XVII
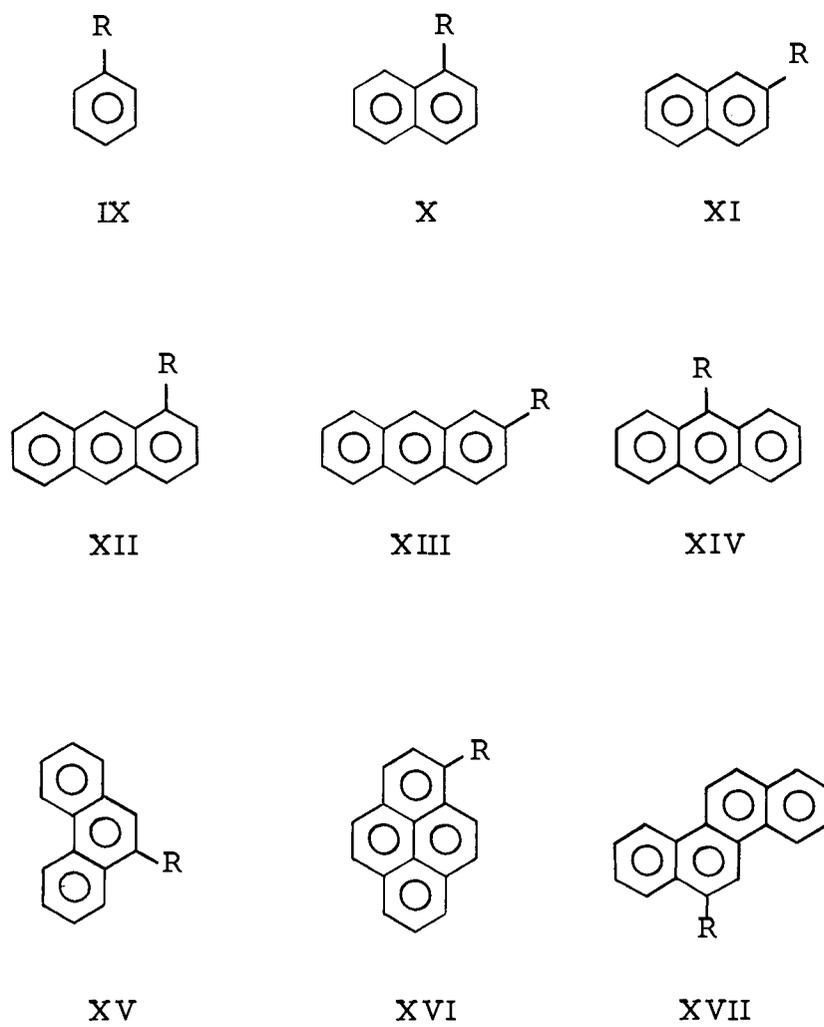
R: CH=CH$_2$

R: C(CH$_3$)=CH$_2$

Figure 4. Structures of polycyclic arenes.

and pyrene derivatives). The two methods were necessary because the anthracene and pyrene derivatives underwent photolytic reactions and phenanthrene was subject to ring phenylation with benzoyl peroxide. The reactivity ratios were calculated by the indirect method (Experimental Section) since a number of the vinylarenes readily polymerized under glc analysis conditions. In this method, only the disappearances of the reference olefin, which did not polymerize under these conditions, and the thiophenol were monitored. Table 6 contains a summary of these results, along with various quantities of these systems calculated by the molecular orbital method. Table 7 is a compilation of the various correlations that were attempted. Figure 5 shows the correlations between the relative reactivities and the calculated total energy changes. The data for 9-vinylanthracene has been omitted from all of the correlations.

Table 6. Relative reactivities of vinylarenes towards thiophenol at 70.0°C.

Compound (Fig. 4 R: CH=CH₂)		Solvent	k_X/k_{Std} [a]	$\Delta\Delta E_{Total}$ [b]	$\Delta\Delta E_{\pi}$ [b]	F [c]
Phenyl	(IX)	Benzene	0.91±0.14 [d]	0	0	0.7697
2-Naph.	(XI)	Benzene	2.5 ±0.3	0.061	0.044	0.7691
9-Phenanth.	(XV)	Benzene	1.8 ±0.2	0.125	0.099	0.7748
1-Naph.	(X)	Benzene	3.6 ±0.5	0.140	0.083	0.7716
1-Naph.	(X)	Cyclohexane	2.2 ±0.2	0.140	0.083	0.7716
6-Chrys.	(XVII)	Benzene	3.5 ±0.2	0.142	0.118	0.7827
2-Anth.	(XIII)	Benzene	5.4 ±1.2	0.167	0.131	0.7691
1-Anth.	(XII)	Benzene	5.9 ±1.5	0.209	0.143	0.7878
1-Pyr.	(XVI)	Benzene	10.5 ±3.5	0.234	0.098	0.7747
9-Anth.	(XIV)	Benzene	1.6 ±1.2	0.424	0.375	0.7785

a) The standard olefin was p-methoxy- α -methystyrene.
b) In electron volts. Changes relative to styrene
c) Free valence
d) Average deviation

Table 7. Correlations between the reactivities of vinylarenes and calculated quantities.

Quantity Correlated	Slope	Correlation Coeff.
Total Energy Change - Overall	4.06±0.08 [b]	0.932
α -Naphthalene Type Cmpds.	5.61±0.08	0.944
β -Naphthalene Type Cmpds.	4.45±0.07	0.972
Pi-Energy Change (SCF)	5.10±0.15	0.730
Pi- Energy Change (HMO)	2.53±0.13	0.858
Total Energy Change - Cation (See Discussion)	0.69±0.16	0.802
Free Valence	16.7 ±0.20	0.349

a) Excluding data for 9-vinylanthracene

b) Average deviation
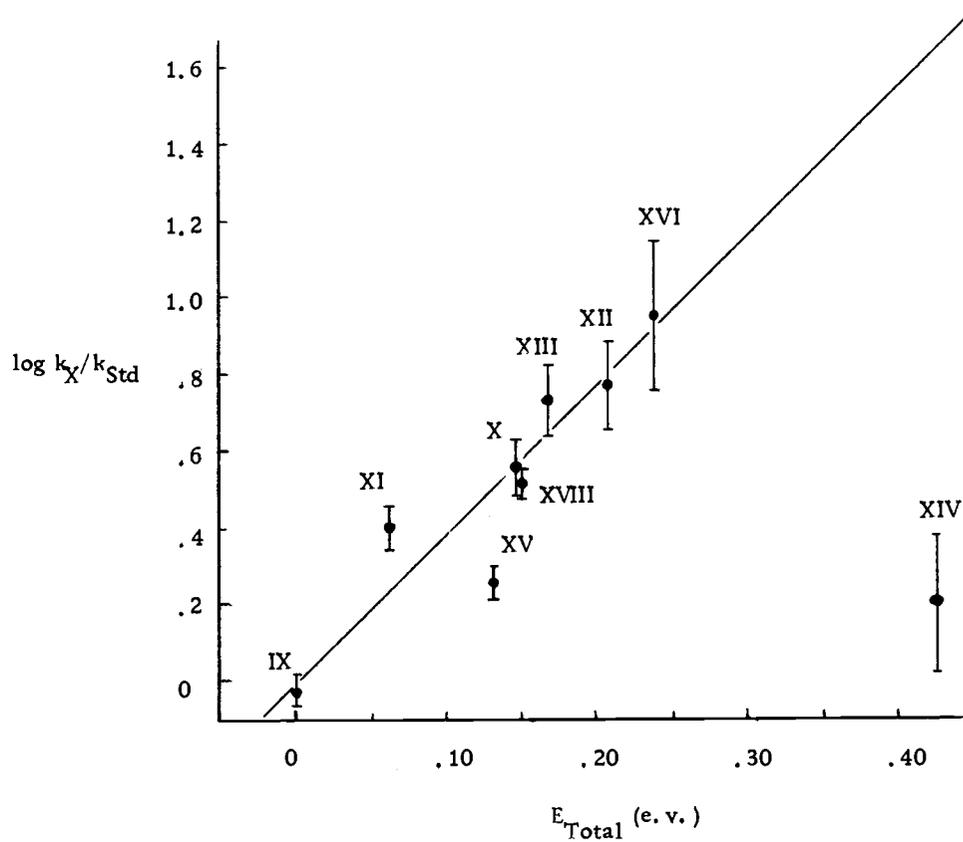
Figure 5. Correlation of log k_X/k_{Std} and $\Delta\Delta E_{Total}$ for the reaction of vinylarenes with thiophenol.

DISCUSSION OF THE RESULTS

Substituent Effects in the Addition of
Thiophenol to α-Methylstyrene

To summarize the observed results for the addition of thio-

phenol to α-methylstyrene, electron-donating substituents in either

$$PhC(CH_3)=CH_2 + PhSH \longrightarrow PhC(CH_3)HCH_2SPh \qquad \text{(Eq. 43)}$$
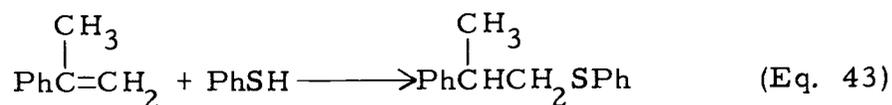
ring enhance the rate of reaction, while electron-withdrawing sub-

stituents retard it. The generality of this conclusion will be discussed

further.

Before proceeding to consider these results in detail, however,

it might be useful to examine the free energy changes that occur in

the course of the attack and chain transfer steps. The reaction

described will be that of thiophenol with styrene. A larger amount

of data exists for this system than for the homolog. The effect

$$PhCH=CH_2 + PhS\cdot \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} Ph\dot{C}HCH_2SPh \qquad \text{(Eq. 44)}$$

$$Ph\dot{C}HCH_2SPh + PhSH \overset{k_{ct}}{\longrightarrow} PhCH_2CH_2SPh + PhS\cdot \qquad \text{(Eq. 45)}$$
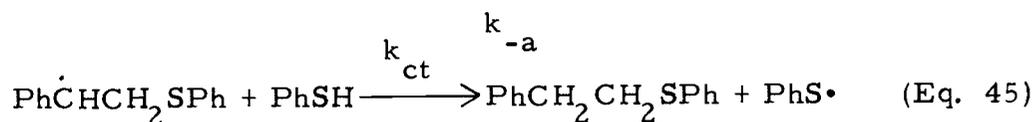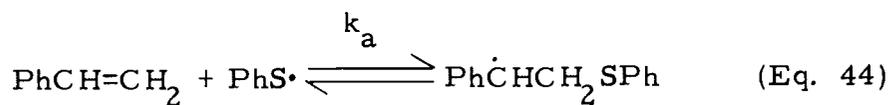
of adding the methyl group to styrene to give α-methylstyrene should

be merely to lower the energy of the carbon-centered radical inter-

mediate slightly. Using the group additivity method and values of

Benson (78, 79), ΔH and ΔS for the addition (gas phase, 25°C) can

be estimated to be -5. 5 kcal/mole and -20 cal/mole-°K, respectively.

The analogous values for the chain transfer are -10. 9 kcal/mole and

-2 cal/mole-°K. An estimation of the activation energy for the chain

transfer step can be made from the data of Sivertz et al. (15, 22)

to be about 3 kcal/mole. The activation barrier for the addition step

can also be estimated from their data to be less than 1 kcal/mole.

Based on these values, a plot of free energy versus the reaction co-

ordinate can be drawn (Figure 6, solid line). From this kind of

plot, it is clear that the addition step should probably be regarded

as a facile equilibrium (with $K_a = k_a/k_{-a}$) occurring prior to the

rate-determining chain transfer.
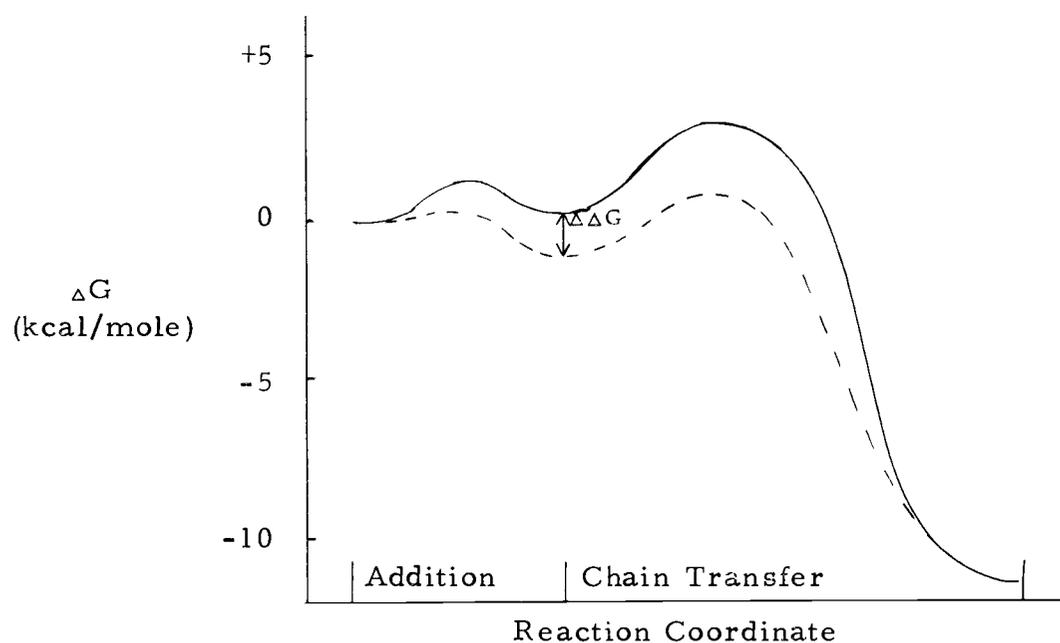
Figure 6. Plot of free energy vs. reaction coordinate for the
addition of thiophenol to styrene.

What then do these observed relationships between structure and reactivity mean? Consider first the experiments in which changes to the olefin moiety were made. As shown in Figure 6, changes that affect the stability of the carbon-centered radical intermediate (the "product" of the addition step) in turn affect the following chain transfer transition state and thus, the activation energy for the overall process. The energy change in the intermediate that corresponds to its variation in stability is approximately $\Delta\Delta G$, the difference between the reaction free energies (for either the addition or chain transfer steps) of the two olefins. This $\Delta\Delta G$ term is related to the addition process by

$$\Delta\Delta G_{12} = A \log \left(\frac{K_{a1}}{K_{a2}} \right) \qquad \text{(Eq. 46)}$$

for olefins 1 and 2. The arguments of Evans and Polanyi (56) assert that a linear relationship exists between the free energy change of the transition state and that of the reaction. The following relation can, therefore, be derived

$$\Delta\Delta G_{12} = B \, (\Delta\Delta G_{12}^{\ddagger}) = C \log \left(\frac{k_{a1}}{k_{a2}} \right) \qquad \text{(Eq. 47)}$$

where k_{a1} and k_{a2} are the forward rate constants of the addition processes. The same reasoning would, of course, also lead to an

equation involving the reverse rate constants, k_{-a1} and k_{-a2}.

Being able to relate the forward rate constants to the activation energy is necessary, since the rate of the forward addition can clearly be treated as a pseudo first order case.

$$R_a = k_a \ (RS\cdot) \ (M) \qquad\qquad (Eq. \ 48)$$

This stipulation is needed if simple competitive experiments are to be used to determine the ratio of the rate constants. The relative reactivities of the olefins treated in this work, then, primarily reflect the sensitivity of the addition step to substituent changes.

The treatment for substituent variations in the thiophenol moiety is much more straightforward. The rate of the chain transfer step (rate-determining) is

$$R_{ct} = k_{ct} \ (A\cdot) \ (RSH) \qquad\qquad (Eq. \ 49)$$

This is also a first order relation, provided that the nature of the carbon-centered radical $(C\cdot)$, as well as its concentration, remains essentially constant. These are, it is believed, reasonable assumptions. Since the substituted thiophenoxy group is insulated from this radical by a methylene group, the effects of such substitution upon reactivity or concentration should be minimal. It is felt, therefore, that changes in the reactivity of thiophenol moiety reflect mainly, changes in the activation energy of the chain transfer step.

$$CH_3$$
$$CHCH_2S$$

Cl

X
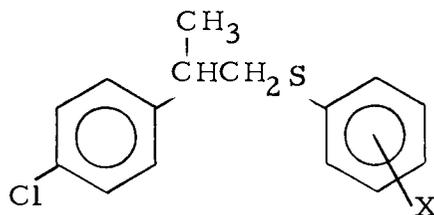
The magnitude of the rho value of -0.38 obtained by correlation of the relative reactivities of substituted α-methylstyrenes with the sigma-plus parameters is in qualitative and semi-quantitative agreement with earlier data (38, 40, 41, 45, 81) if differences in temperature, solvent, and the nature of the radicals are taken into account. Certainly it is a reasonable sensitivity for such a facile process.

That the observed sensitivity may depend significantly on the solvent can be shown by comparing the relative reactivities of 1-vinyl-naphthalene in benzene and cyclohexane- the value in the former solvent (a complexing solvent) is 1.6 times greater, indicating a greater selectivity of the attacking radical. The work of Russell has clearly shown a dependence of the observed selectivity in radical reactions upon the complexing ability of the solvent (82-85). That such complex formation could occur between the attacking radical and aromatic substrates has been demonstrated by Martin and Gleicher (86, 87). It is felt that, while such complexation is undoubtedly taking place in the present study, concentration factors

will cause complexation between the attacking thiyl radical and the benzene solvent to predominate. This should give rise to a constant effect on the observed selectivity. Thus, in comparing the rho value from this study to the others, it must be remembered that a portion of the observed selectivity will be attributable to complexation and that the value here determined is probably larger than the "true" sensitivity of the reaction. Of course, complexation will also have an effect upon the rho value determined for the reaction of substituted thiophenols with p-chloro-α-methylstyrene.

In view of the substantial exothermicity of the charge transfer step, a rho value as small as -0.27 is not really surprising. This is a smaller value than that obtained by Kooyman et al. (77) for hydrogen abstraction from substituted thiophenols by 1-cyano-1-cyclohexyl radical, but again, variations in experimental conditions and the nature of the species involved undoubtedly play a large role in determining the observed sensitivity.

There is an additional point regarding the value of rho for the chain transfer step obtained in this study. Certainly the nature of the substituent in the α-methylstyrene system will affect the selectivity and polar character (vide infra) of this radical. The rho value will change as the characteristics of the abstracting radical change. However, the useful information that is gained from this is not so much the magnitude of rho, but it is rather whether or not there is

in fact a linear free energy relationship at all.

Another major question which arises from the results herein presented is whether they demonstrate the polar nature of the transition states of the addition and chain transfer steps. On the basis of the better correlations with the sigma-plus parameters in both studies, it is felt that the transition states involve considerable contributions from the polar forms shown below. Again, the results in the latter case may be due to the selection of an α-methylstyrene

$$\left[\begin{array}{c} \underset{\mid}{CH_3} \\ PhC{=}CH_2 \cdot SPh \end{array} \longleftrightarrow \begin{array}{c} \underset{\mid}{CH_3} \\ Ph\underset{\bullet}{C}CH_2SPh \end{array} \longleftrightarrow \begin{array}{c} \underset{\mid}{CH_3} \\ Ph\underset{+\bullet}{C}CH_2\,{:}SPh \end{array} \right]^{\ddagger}$$

$$\left[\begin{array}{c} \underset{\mid}{CH_3} \\ PhSH \ \ {\bullet}CPh \\ \underset{\mid}{CH_2SPh} \end{array} \longleftrightarrow \begin{array}{c} \underset{\mid}{CH_3} \\ PhS{\cdot}\ HCPh \\ \underset{\mid}{CH_2SPh} \end{array} \longleftrightarrow \begin{array}{c} \underset{\mid}{CH_3} \\ Ph\overset{+}{S}\ \overset{-}{H}\ {:}CPh \\ \underset{\mid}{CH_2SPh} \end{array} \right]^{\ddagger}$$
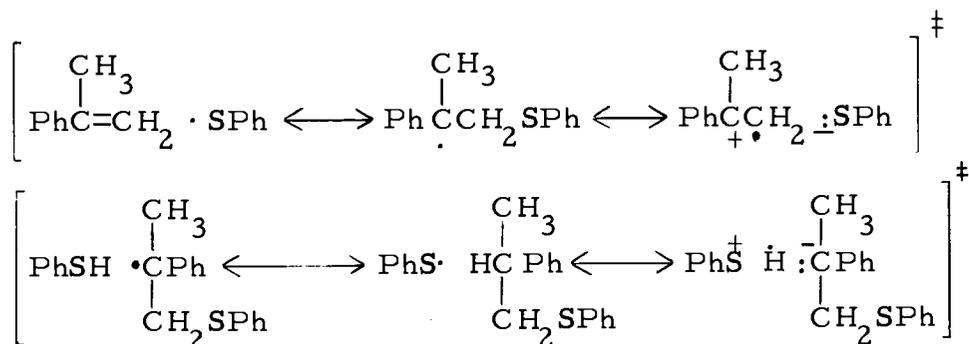
to react with the substituted thiophenols that is probably fairly electron-withdrawing by virtue of the chlorine substituent. The point is that for this particular system a polar structure is clearly indicated on the basis of a close correlation with the sigma-plus parameters.

The relative rate observed for p-nitro-α-methylstyrene deserves some comment. A similar enhanced reactivity towards trichloromethyl radicals for styrenes substituted in the para position has been attributed to extra resonance stabilization of the transition

state (38). Another explanation is also available that seems to better

fit in with the present results. Walling et al. have shown that elec-

tron-withdrawing groups (especially para ones) increased the reac-

tivity of styrene towards copolymerization (81). In addition, it has

been shown in this study that a small amount of thiophenol reacted

with more than twice the stoichiometric amount of p-nitro-α-methyl-

styrene. Also in this study, no upward deviation of the para electron-

donating group derivatives were observed. It is felt, therefore,

that the high reactivity of α-methylstyrenes and styrenes substituted

with strong electron-withdrawing groups in the para position may

be a result of competing copolymerization of those compounds.

Correlations with Calculated Parameters

Several initial points need to be made with regard to the choice

of the system. The initial project called for the use of isopropenyl-

arenes. However, after a number of kinetic experiments (see

Results), it became apparent that steric factors were playing a

major role in determining the relative rates of addition. This can

most easily be seen in Table 5 by comparing the large relative rates

for "2-naphthalene-type" compounds to the much lower ones for

"1-naphthalene-types." Clearly, nonbonded interactions of the sort

H H
H C CH$_2$SPh
H C
H

must be forcing the intermediate radical from planarity, thus reduc-

ing delocalization stabilization and decreasing the rate.

While such steric effects are interesting, they do present extra

variables that must be incorporated into any correlations of the

relative rates with calculated parameters. The shift to the vinyl-

arenes was then made to escape nonbonded interactions, since the

intermediate in this case could adopt a planar conformation.

H · CH$_2$SPh
C
H

Although this switch might now bring into play increased poly-

merization by the secondary carbon-centered radical, the results

do not bear this out. In specific product analyses, no polymeric

products were observed. However, polymerization under glc analy-

sis conditions did necessitate a different method of anlaysis based

on the disappearance of thiophenol and a reference olefin. While

this method is less exact and does give rise to increased scatter of

the data points, it is still a valid way of monitoring the reaction in view of the result that no disulfide was observed with the products. Also, ring substitution does not appear to be a particular problem. As a test of this, the original data for the α-methylstyrenes were reexamined. A rho value of -0. 36 ± 0. 08 was determined. This is in reasonable agreement with the original value of -0. 38±0. 02. The data may be found in Table 1. Figure 2 may be compared to Figure 1.

Several aspects relating to reactions of the anthracene and pyrene systems need to be discussed. Because of known photolytic dimerizations, an alternative method of initiation of these compounds was required. Benzoyl peroxide decomposition was the method of choice. The only drawback with this form of initiation was the large experimental uncertainty that seemed to occur for the values of the relative rates.

Another problem with the anthracene is the known nuclear addition of thiophenol to the meso positions of that ring system (88-91). However, this reaction does not seem to be significant under the present conditions. In a period comparable to a kinetics experiment, less than 5% of the stoichiometric amount of thiophenol and anthracene reacted.

With the exception of 9-vinylanthracene (vide infra), a reasonable correlation of the relative rates with the calculated total energy differences between the starting olefin and the corresponding

carbon-centered radical intermediate was obtained. The interpretation of this result is essentially the same as that put forward previously for the addition of thiophenol to substituted α-methylstyrenes. The calculated energy differences should reflect the relative differences in free energies (entropy assumed constant) for the addition step. These in turn reflect the variation in activation energy for that process.

It is possible that the better correlations observed when the data is divided into two groups corresponding to those compounds resembling 1-vinylnaphthalene (X, XII, XV, XVI, XVII) and those resembling 2-vinylnaphthalene (IX, XI, XIII) indicate different steric requirements of these two types of compounds (75). There may be significant nonbonded interactions in the 1-naphthyl types that are not present in the 2-naphthyls. However, in view of the large degree of uncertainty of these results, it is inappropriate to draw such conclusions.

Several other parameters were utilized in attempts to correlate with the experimental reactivities. All failed to do so. One interesting case is the attempted correlation with the total energy change calculated by taking the difference between the starting vinylarene and the carbonium ion "formed" by the removal of the odd electron from the carbon-centered radical.

$$Ar-C\begin{array}{c} H \\ \diagup \\ \diagdown \\ CH_3 \end{array} +$$
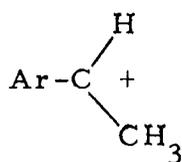
While this is one of the best of the "other" parameters in correlating

with the reactivities, the correlation coefficient is only 0.802. It

may indicate that, while a charged contributing form is important

to the stabilization of the transition state as determined by the ob-

served polar effects, its contribution is still relatively minor com-

pared to the stabilization due to the form similar to the product

radical. Finally, it should be noted that the correlation with the

free valence is very bad, even though this ground state parameter

is closely associated with radical reactivity (53).

As in the earlier study, the SCF-MO approach represents a

considerable improvement over the Hückel method (65). The reac-

tivities of vinylarenes towards thiyl radical in this study gave only

a modest correlation (r=0.858) with the pi-energies determined by

the Hückel approach.

It is interesting to compare the present results with those of

Gleicher and Unruh (65) for hydrogen atom abstraction from methyl-

arenes. The free energy for the addition step is probably closer to

thermoneutrality than is that for the abstraction from arylmethanes

by the trichloromethyl radical. The addition process also has a

much lower activation barrier. Thus, while a dependence of the

rate upon the ability of the aromatic system to delocalize the odd electron in the transition state is clearly indicated, the facile nature of the step requires less such stabilization. Therefore, for the addition reaction the slope of the correlation of log "relative rate constant" _versus_ the calculated relative energy difference is seen to be less than in the case of abstraction by trichloromethyl radical from methylarenes. The marginal correlation coefficient may well be due to the large experimental errors that are associated with the relative rate data.

Comparing the molecular orbital methods, the present study incorporated the variable bond length approach (63) and thus, a calculation of the sigma-bond energy is possible. The energy difference, then, contains both sigma- and pi-energy components. The importance of the sigma-component to the total energy can be seen in the poor correlation of the relative rates with just the pi-energy differences.

Anomalously, 9-vinylanthracene is much less reactive than would be expected solely on the basis of the other data. Apparently, the steric interaction is more severe in this case. No planar structure is possible which will not show a large _peri_ interaction. LeFevre _et al._ have determined that the angle between the plane of the vinyl group and the plane of the anthracene in 9-vinylanthracene is 60° (92). Using this conformation to calculate the energies of
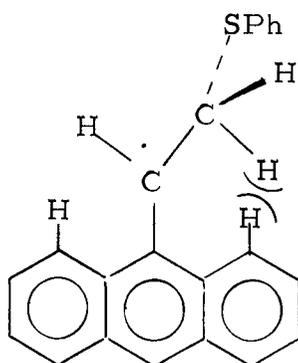
the olefin and the radical gave a predicted energy change of -0.110 e. v.

relative to styrene. This corresponds to a predicted reactivity that

is much lower than what is experimentally observed. Such a discrep-

ancy may reflect either the error in the determination of the confor-

mation of 9-vinylanthracene or that the greater dependence of the

radical system upon delocalization may reduce the deformation angle

somewhat at the expense of increased nonbonded interactions which

are not explicitly incorporated into the molecular orbital treatment.

A few final words are in order concerning the attempts at

studying thiol addition to vinylpyridines. The results seem

to indicate that the nucleophilic nitrogen is a problem. For thio-

phenol addition to p-methoxy-α-methylstyrene, experiment shows that

the reaction is certainly catalyzed by the presence of pyridine. This

may well be due to some sort of enhanced proton transfer by the

basic pyridine. It should also be noted that attempted hydrogen

abstraction from methylpyridines by bromine atom or trichloro-

methyl radical also failed. Experiments with pyridine itself indicate

probable substitution at the nitrogen atom under the reaction conditions employed.

EXPERIMENTAL

All melting points were determined using a Mel-Temp apparatus and unsealed glass capillaries. All values are uncorrected. The nmr spectra were run on either a Varian HA-100 or EM-360. Chemical shifts are expressed as parts per million (δ) from tetramethylsilane internal standard. Solvents will be noted in the tables. IR spectra were determined on a Beckman IR-8, the samples being either a film between NaCl discs or formed into pellets with KBr. Indices of refraction were found using a Bausch and Lombe Abbé refractometer at the indicated temperatures. All glc analyses were performed on a Varian Aerograph model 202B equipped with a thermal conductivity detector and using helium as the carrier gas. A disc integrator on the Sargent recorder was used to determine the peak areas. Most experiments were carried out using a $\frac{1}{4}$ inch x 12 foot aluminum column packed with 5% SE-30 on Chromosorb W (AW, DMCS), although occasionally a $\frac{1}{4}$ inch x 12 foot aluminum column of 8% FFAP on Chromosorb W (AW, DMCS) was needed for better separation.

Purification of Reagents

The purity of all of the following reagents, as determined by gas-liquid chromatography and, in some cases, by nmr, was greater than 98%.

Benzene. Reagent grade benzene (Matheson Coleman and Bell) was used after distillation at 80°C. It was then stored over sodium wire.

o-Dichlorobenzene. The reagent (Matheson Coleman and Bell) was stored over Linde molecular Sieve (Allied Chemical). No further purification was done prior to its use.

Chlorobenzene. Reagent grade (Matheson Coleman and Bell) was used without further purification.

Cyclohexane. Spectroquality cyclohexane (Matheson Coleman and Bell) was used without additional purification.

Benzoyl peroxide. Granular benzoyl peroxide (Matheson Coleman and Bell) was used without further purification.

Thiophenol. Thiophenol (Aldrich) was distilled at atmospheric pressure. The fraction boiling from 168-9°C was used in the kinetics experiments.

α-Methylstyrene. The commercial product (Aldrich) was used after distillation at 160-1°C (760 torr). The nmr spectrum can be found in Table 9.

9-Vinylanthracene. The commercial product (Pfaltz and Bauer) was used without further purification. Physical properties and the nmr spectrum can be found in Tables 12 and 13, respectively.

p-Chlorothiophenol. This compound (Aldrich) was used as supplied.

p-Methoxythiophenol. The commercial product was distilled prior to use. B. p. 100°C at 10 torr.

p-Methylthiophenol. p-Methylthiophenol (Aldrich) was distilled. B. p. 110°C at 10 torr.

Preparation of Compounds

In those situations where a common procedure was followed for a number of compounds, only one description of the method will be given, although variations and specific problems will be mentioned. Unique syntheses of individual compounds will, of course, be treated separately. The physical properties, overall yields, and nmr data are tabulated at the end of each section.

Preparation of Substituted α-Methylstyrenes

The preparation of all but one of the substituted α-methylstyrenes proceeded through a cumyl alcohol formed by the addition of a Grignard reagent to a ketone, water then being eliminated to give the olefin. The exception to this general procedure was p-nitro-α-methylstyrene, since the nitro group and Grignard reagents are incompatible. The specific procedure for the p-nitro derivative follows that for the generalized procedure.

General procedure for p-methoxy-, p-methyl-, m-methyl-,
m-methoxy-, p-chloro-, m-chloro-, and m-trifluoromethyl-α-
methylstyrene. Scheme I shows the synthetic steps involved. The
p-methoxy compound was made starting with p-methoxyacetophenone
in ether. To this, excess methylmagnesium iodide in ether was
added with cooling and in a nitrogen atmosphere. The resulting sus-
pension was then stirred at room temperature overnight. The initial
reaction for the other compounds (p-methyl, m-methyl, m-methoxy,
p-chloro, m-chloro, and m-trifluoromethyl) involved reacting the
appropriately substituted bromobenzene with a slight excess of
magnesium in ether and under nitrogen, followed by 4-8 hours of
reflux. A stoichiometric amount of dry acetone was then added and
the suspension of adduct was stirred for about one hour.

At this point, then, the magnesium salt suspension was poured
onto excess crushed ice. In the case of two of the compounds (m-
methyl and m-methoxy) acid was added to neutralize the basic solu-
tion. The aqueous layer was then extracted with ether. In the other
preparations, the aqueous slurry of magnesium salts was extracted
directly with ether. In all cases, the ether solution was then dried
over magnesium sulfate, filtered, and evaporated to yield crude
alcohol.

The crude alcohol was next dehydrated either by simple distilla-
tion at atmospheric pressure (m-methyl and m-methoxy) or by

distillation from fused potassium bisulfate at reduced pressure. The

olefin thus obtained was then redistilled prior to use in the kinetics

experiments.

Procedure for p-nitro-α-methylstyrene. This compound was

prepared according to the procedure of Okamoto and Brown (93) as

shown in Scheme II. Cumene (40 g. , 0. 33 mole) was slowly added

to a solution made from 50 g. of nitric acid and 74 g. of sulfuric acid,

making sure that the temperature remained below 35°C. This mix-

ture was then poured into excess cold water. The resulting organic

layer was next separated, then washed with water, dried over calcium

chloride, filtered and distilled (b. p. 100-110°C at 25 torr). The

yield of p-nitrocumene was 50%. That material and N-bromo-

succinimide in stoichiometric ratio, together with a trace of benzoyl

peroxide, were refluxed in carbon tetrachloride for 7 hours. The

succinimide was filtered off and the solvent was removed. The

resulting oil was then distilled under reduced pressure to yield the

crude p-nitro-α-methylstyrene formed by elimination of HBr during

the distillation. Recrystallization from ethanol/water gave the pure

compound characterized in Tables 8 and 9.

Preparation of p-Nitrothiophenol

The method of Price and Stacey was used to prepare p-nitro-

thiophenol (100). To a solution of excess p-chloronitrobenzene in

Table 8. Summary of the physical properties and overall yields for the substituted α-methylstyrenes.[a]

Substituent	B. P. $_{Torr}$/M. P. (°C)	n_D^{Temp}	Yield (%)	Ref.
none	b. p. $160\text{-}1_{760}$ $(161\text{-}2_{760})$	1.5377^{21} (1.5311^{24})	--	94
m-Cl	b. p. $100\text{-}10_{20}$ $(60\text{-}2_4)$	1.5546^{21} (1.5536^{20})	69	95
p-Cl	b. p. $105\text{-}20_{20}$ $(80\text{-}3_{10})$	1.5567^{21} (1.5529^{25})	56	96
m-CH$_3$	b. p. $180\text{-}90_{760}$ $(86\text{-}9_{25})$	1.5289^{22} (1.5335^{20})	58	97
p-CH$_3$	b. p. $187\text{-}94_{760}$ $(76\text{-}8_{19})$	1.5352^{22} (1.5290^{25})	68	96
m-CH$_3$O	b. p. $215\text{-}17_{760}$ (---)	1.5419^{22} (---)	25	--
p-CH$_3$O	m. p. 30-1 (32)	--	8.5	98
p-NO$_2$	m. p. 48-50 (51-52)	--	8.5	93
m-CF$_3$	b. p. $100\text{-}10_{25}$ $(83\text{-}4_4)$	1.4648^{22} (1.4635^{25})	54	99

a) Literature values in parentheses

Table 9. Summary of nmr data for substituted α-methylstyrenes in carbon tetrachloride.[a]

$$Ha_3C-C=C\begin{array}{c}H_b\\H_c\end{array}$$
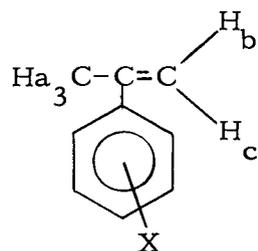
Substituent	H_a [b]	H_b [b]	H_c [b]	$H_{aromatic}$ [b]	H_X [b]
p-CH$_3$O	2.08	4.86	5.23	6.69/7.25	3.39
p-CH$_3$	2.10	4.96	5.27	7.00/7.25	2.29
m-CH$_3$	2.11	4.99	5.27	6.87-7.31	2.31
H	2.08	5.00	5.30	7.16-7.44	--
m-CH$_3$O	2.11	5.06	5.35	6.71-7.32	3.40
p-Cl	2.08	5.02	5.28	7.02-7.40	--
m-Cl	2.07	5.05	5.30	7.07-7.36	--
m-CF$_3$	2.13	5.13	5.38	7.24-7.77	--
p-NO$_2$	2.19	5.24	5.46	7.56/8.14	--

a) In all cases, the experimental and calculated proton ratios agreed within 5%

b) Chemical shift from TMS in ppm δ

ethanol, an ethanolic solution containing equimolar amounts of sodium sulfide and sulfur was added. After a few minutes, a 1.5 N solution of sodium hydroxide in ethanol was added and the mixture boiled for 20 minutes. This mixture was cooled and poured onto ice. The aqueous solution was then filtered and acidified. The resulting solid was filtered, taken up in basic ethanol, reprecipitated with aqueous mineral acid, and filtered. This yielded pure product on recrystallization from aqueous ethanol. m.p. 72-4°C (lit. 75°) Yield: 15%.

Preparation of Isopropenylarenes

General procedure for 1- and 2-isopropenylnaphthalene and 9-isopropenylanthracene. To a two-fold excess of magnesium turnings in refluxing ether was added an etheral solution of 9-bromoanthracene. Heating at reflux was continued for 22 hours. Acetone was then added to the cooled Grignard reagent.

In the cases of the naphthalenes, excess methylmagnesium iodide was added to a solution of the appropriate naphthylmethyl ketone, as before.

The usual work up gave crude 2-arylpropan-2-ols. The anthracene derivative so obtained was then dehydrated by boiling the alcohol with a catalytic amount of iodine in toluene, using a Dean-Stark apparatus to remove water as it was formed. Fused

potassium bisulfate was used to eliminate water from the naphthalene derivatives. A second distillation was then carried out.

Procedure for 9-isopropenylphenanthrene. A Wittig reaction (Scheme IV) was used to prepare 9-isopropenylphenanthrene. A stoichiometric amount of methylphosphonium bromide was added to a solution of phenyllithium in tetrahydrofuran. After stirring and refluxing several hours, slightly less than the stoichiometric amount of 9-acetylphenanthrene was added. The resulting solution was refluxed for 18 hours, cooled, diluted with ethyl ether, and washed with water. Upon drying, filtering, and evaporating, an oil was obtained that was about 70% product, the remainder being unreacted starting material. This mixture was separated on an alumina column by elution with hexane. The greenish oil thus obtained was distilled to yield the product cited in the tables.

Table 10. Summary of physical properties and overall yields of the isopropenylarenes.[a]

Compound	B. P.$_{torr}$/M. P. ($^{\circ}$C)	n_D^{temp}	Yield (%)	Ref.
1-naph.	b.p. 85-100$_1$ (114-5$_5$)	1. 6053^{25} (1.6137^{20})	78	101
2-naph.	m. p. 52-3 (56)	--	83	102
9-phenan.	b.p. 112-6$_{.05}$ (163$_{20}$)	-- (1.6765^{22})	24	103
9-anth.	m.p. 81-3 (85-6)	--	13	104

a) Literature values in parentheses

Table 11. Summary of nmr data for the isopropenylarenes in carbon tetrachloride.[a]

$$\underset{Ar}{\overset{H_{a3}C}{\diagdown}}C = C\underset{H_c}{\overset{H_b}{\diagup}}$$

Compound	H_a[b]	H_b[b]	H_c[b]	$H_{aromatic}$
1-naph	2.16	5.00	5.35	7.10-8.00
2-naph.	2.20	5.10	5.50	7.30-7.80
9-phenan.	2.15	5.10	5.30	7.00-8.50
9-anth.	2.30	5.20	5.70	7.20-8.30

a) Experimental and calculated proton ratios agree within 5%.

b) Chemical shift from TMS in ppm δ

Preparation of Vinylarenes

Procedure for styrene and 1- and 2-vinylnaphthalene. The
synthesis of these compounds is very similar to that already described
for the corresponding isopropenylaromatics. The 1-arylethanols
were prepared and then the crude alcohols were distilled from potas-
sium bisulfate at reduced pressure to give the crude olefins. The
1-phenyl- and 1-(1-naphthyl) ethanols were prepared by adding the
appropriate bromide to a slight excess of magnesium in ether under
nitrogen. After several hours at room temperature, excess acet-
aldehyde in ether was added directly to the phenylmagnesium

bromide. The α-naphthyl Grignard was first solubilized with benzene,
after which the acetaldehyde was added. The resulting salts were
hydrolyzed by pouring onto ice and the alcohols were extracted from
the aqueous slurry of magnesium salts with ether. The organic layers
were then dried, filtered, and evaporated to the crude alcohols. To
prepare the 1-(2-naphthyl)ethanol, 2-acetonaphthone was reduced
in ether with excess lithium aluminum hydride. Filtration and
evaporation of the ether layer yielded the alcohol.

For the remaining compounds the approach shown in Scheme V
was utilized. Since there are a number of reactions involved in
the synthesis of each compound, they will be separately described.

Procedure for 1-vinylanthrancene. Benzanthrone was boiled
with excess aqueous sulfuric acid, and chromium trioxide (five-fold
excess) was added slowly (105). This mixture was diluted with hot
water. On cooling, crystals of anthraquinone-1-carboxylic acid
formed. The crude acid was then reduced by a suspension of zinc
dust in aqueous ammonia. After six hours of reflux, the solution
was cooled and filtered. The filtrate was then acidified and the
resulting flocculent precipitate was collected. Recrystallization
from glacial acetic acid gave pure anthracene-1-carboxylic acid in
48% overall yield, m.p. 248-50°C (Reference 106, m.p. 245°C).
The acid was then refluxed in a 5% solution of sulfuric acid in absolute
methanol. After 10 hours, the solution was cooled and methyl

anthracene-1-carboxylate crystallized. The crude yield was 81%,

m. p. 99-100°C (Reference 106, m. p. 104°C). To carry out the

reduction to the alcohol (105), the ester was placed in the thimble

of a Soxhlet extractor, while excess lithium aluminum hydride in

ether was boiled in the lower flask. The crude alcohol (yield: 100%)

was isolated from the ether solution by hydrolysis. It was converted

to the bromide, directly, in chloroform using a slight excess of

phosphorus tribromide, a small amount of pyridine being needed

as a catalyst (107). After hydrolyzing the mixture with crushed ice,

the organic layer was washed with aqueous sodium bicarbonate and

water, dried, filtered, and evaporated. The crude yield for this

step was 100%. To the 1-(bromomethyl)anthracene in toluene was

added to an equimolar amount of triphenylphosphine (107). Refluxing

overnight and cooling gave crystals of 1-anthryl methyltriphenyl-

phophonium bromide which were filtered. The yield was 87%. The

phosphonium salt was then converted into the ylid by an equimolar

amount of phenyllithium. This reaction was carried out at room

temperature under nitrogen in tetrahydrofuran as solvent. After

stirring this mixture for 30 minutes, an excess solution of formalde-

hyde in tetrahydrofuran was added. This mixture was stirred for

12 hours. It was then poured into water and extracted with ether.

The ether layer, after being dried over magnesium sulfate, filtered,

and evaporated, yielded a solid that was extracted with boiling hexane.

After cooling, the hexane was filtered and evaporated. The resulting solid residue was recrystallized from ethanol to give the pure 1-vinylanthracene.

Procedure for 2-vinylanthracene. To a refluxing mixture of 2-methylanthraquinone, an excess of chromium trioxide dissolved in slightly wet acetic acid was added. On cooling, yellow crystals of anthraquinone-2-carboxylic acid were deposited in 64% yield. The reduction to anthracene-2-carboxylic acid was carried out as before, by zinc dust in aqueous ammonia. The same procedures were also used to prepare the methyl ester, the hydroxymethyl- and bromomethyl-derivatives, the phosphonium bromide, and the olefin.

Procedure for 9-vinylphenanthrene. By refluxing an ether solution of magnesium and 9-bromophenanthrene, the desired Grignard was formed (108). To this was added a formaldehyde tetrahydrofuran solution. Standard work up gave the hydroxymethyl compound in 53% yield. From this point, the same procedures outlined above gave 9-vinylphenanthrene, the only difference being the olefin was purified by distillation at reduced pressure.

Procedure for 1-vinylpyrene. Pyrene-1-carboxylic acid was prepared by the hypochlorite oxidation of 1-acetylpyrene (109). An excess solution of potassium hypochlorite was heated to a gentle reflux and 1-acetylpyrene was added. Reflux was continued for another 9 hours. The solution was cooled to room temperature and

extracted with ether. Evaporation of this ether layer yielded 71%

of the crude acid. Next, the acid was added to a suspension of

excess lithium aluminum hydride in tetrahydrofuran. Normal work

up gave the alcohol in 100% yield. The usual procedures then led

to 1-vinylpyrene.

Procedure for 6-vinylchrysene. A benzene/ether solution of

6-bromochrysene was treated with an equivalent amount of phenyl-

lithium to give 6-chrysyllithium. Solid carbon dioxide was added

to this solution. After hydrolysis with saturated ammonium chloride

solution, the organic layer gave up 13% of the chrysene-6-carboxylic

acid. The standard method then gave 6-vinylchrysene.

Table 12. Summary of physical properties and overall yields of vinylarenes.[a]

Compound	B.P.$_{torr}$/M.P. ($^{\circ}$C)	n_D^{temp}	Yield (%)	Ref.
Styrene	b.p. 100-10$_{50}$ (145-6$_{760}$)	1.5430^{25} (1.5463^{20})	48	110
1-Naph.	b.p. 79-80$_{.45}$ (115-6$_4$)	1.6411^{25} (1.6436^{20})	12	111
2-Naph.	m.p. 64-6 (66)	--	26	112
1-Anth.	m.p. 53-6 (58-61)	--	4.2	104
2-Anth.	m.p. 185-9 (187-8)	--	4.7	104
9-Anth.	m.p. 60-3 (64-7)	--	--	104
9-Phenanth.	b.p. 140$_{.1}$ (194-7$_6$)	--	10	113
1-Pyr.	m.p. 82-4 (87-9)	--	20	114
6-Chrys.	m.p. 138-40	--	2.8	--

a) Literature values in parentheses

Table 13. Summary of nmr data for the vinylarenes in deuterochloroform.[a]

$$\begin{array}{c} H_c \qquad H_a \\ \diagdown \diagup \\ C = C \\ \diagup \diagdown \\ Ar \qquad H_b \end{array}$$

Compound	H_a[b]	H_b[b]	H_c[b,c]	$H_{arom.}$[b]
Styrene	5.16 (J_{ab}=1)	5.66 (J_{bc}=18)	6.65 (J_{ac}=10)	7.00-7.45
1 - Naph.	5.36 (J_{ab}=1)	5.65 (J_{bc}=18)	-- (J_{ac}=10)	7.20-7.45
2-Naph.	5.25 (J_{ab}=1.5)	5.75 (J_{bc}=18)	6.80 (J_{ac}=10)	7.20-7.70
1-Anth.	5.41 (J_{ab}=1.5)	5.74 (J_{bc}=17)	-- (J_{ac}=11)	7.10-8.67
2-Anth.	5.40 (J_{ab}=0)	5.93 (J_{bc}=17)	6.97 (J_{ac}=11)	7.40-8.46
9-Anth.	6.00 (J_{ab}=2)	5.63 (J_{bc}=17)	-- (J_{ac}=11)	7.33-8.50
9-Phenanth.	5.34 (J_{ab}=2)	5.69 (J_{bc}=16)	-- (J_{ac}=11)	7.01-8.55
1-Pyr.	5.49 (J_{ab}=2)	5.87 (J_{bc}=17)	-- (J_{ac}=11)	7.48-8.39
6-Chrys.	5.60 (J_{ab}=2)	6.00 (J_{bc}=16)	-- (J_{ac}=11)	7.20-9.00

a) Experimental and calculated proton ratios agree within 5%

b) Chemical shift from TMS in ppm δ.   Coupling constants in Hz. in parentheses

c) Often partially buried in the "aromatic" signal

Procedure for the Analysis of the Reaction
between α-Methylstyrene and Thiophenol

α-Methylstyrene (50.0 mmoles) and thiophenol (50.0 mmoles)

in 25 ml of benzene were refluxed for one hour while being photolyzed

through the pyrex equipment with a 275-watt sunlamp. The solution

was then cooled and extracted with 0.1 N potassium hydroxide. The

benzene layer yielded an oil which consisted (by glc) of 6.4% α-methyl-

styrene and one other component having considerably longer retention

time. Purification by distillation under reduced pressure showed

that this latter material was the sulfide adduct resulting from the

anti-Markownikoff addition, b.p. 95-100°C at 20 torr. Nmr: 1.35

ppm δ, doub., 3.0 H; 3.00 ppm δ, mult., 3.0 H; 7.15 ppm δ, mult.,

10.7 H.

Procedure for the Analysis of the Reaction between
p-Methoxy-α-methylstyrene and Thiophenol

The procedure described above was repeated using p-methoxy-

α-methylstyrene. The sulfide distilled at 230°C (20 torr). Nmr:

1.35 ppm δ, doubl., 3.0 H; 2.95 ppm δ, mult., 3.0 H; 3.70 ppm δ,

sing., 3.7 H; 6.7-7.3 ppm δ, mult., 9.7 H.

The experiment to determine the extent of polymerization was car-

ried out as for the kinetics runs (vide infra). A solution was prepared

from p-methoxy-α-methylstyrene (6.36 mmoles), thiophenol (4.84

mmoles), o-dichlorobenzene (5.09 mmoles), and benzene (2.81

mmoles). The o-dichlorobenzene was incorporated as an internal

standard for glc analysis. This solution was divided into eight

ampoules that were deoxygenated and sealed under low pressure

nitrogen. Six of these ampoules were reacted at 70.0°C for one

hour. The observed number of mmoles of p-methoxy-α-methyl-

styrene reacting was 4.94±0.04 mmoles. Based on the reaction of

thiophenol, this number of mmoles should be 4.70±0.05 mmoles,

assuming that thiophenol disappears only by way of the addition

reaction. The difference between these two values, 0.24±0.09

mmoles, represents the maximum amount of the olefin that dis-

appeared via polymerization. The percentage of the initial olefin

that disappeared by polymerization was no greater than 4.8±0.2%.

Procedure for the Analysis of the Reaction between p-Nitro-α-methylstyrene and Thiophenol

The olefin (3.59 mmoles) and thiophenol (0.11 mmoles) were

reacted as above for 140 minutes at 70.0°C. Reacted and unreacted

samples were then analyzed by glc. Based on the disappearance of

the p-nitro-α-methylstyrene peak, the number of mmoles of olefin

that reacted was 0.23 (Average % reaction = 6.5).

Procedure for the Analysis of the Reaction between
1-Vinylnaphthalene and Thiophenol

A mixture of 1-vinylnaphthalene (6. 60 mmoles), thiophenol

(10. 3 mmoles), and benzene (338 mmoles) were photolyzed at 70. 0°C

for 2 hours. Work up was as before. The only observed product was

purified by distillation at reduced pressure. The distillate solidified

on standing to a white, crystalline material, m. p. 37-40°C. Nmr:

3. 25 ppm δ, mult. , 4. 0 H; 7. 1-7. 9 ppm δ, mult. , 12. 7 H. Analysis

(Theoretical): C - 82. 03 (81. 77); H - 6. 20 (6. 10); S - 12. 27 (12. 13).

Procedure for Studying the Overall Reversibility
of the Addition of Thiophenol
to α-Methylstyrene

A mixture of 1-thiophenoxy-2-phenyl propane (4. 83 mmoles),

p-methoxy-α-methylstyrene (4. 78 mmoles), o-dichlorobenzene

(4. 60 mmoles), and benzene (29. 10 mmoles) were photolyzed to-

gether as in the kinetic experiments at 70. 0°C. Based on the sulfide

peak (since a small amount of the olefin might disappear via poly-

merization) in the glc trace, no exchange occurred within experi-

mental uncertainty (% reaction of sulfide = 2. 4±3. 6%).

Procedure to Determine the Extent to which Pyridine Catalyzes a Reaction between p-Methoxy-α-methylstyrene and Thiophenol

Two solutions were made up. Both contained p-methoxy-α-methylstyrene, thiophenol, and o-dichlorobenzene in benzene. Pyridine was added to one of the solutions. The approximate ratio of olefin:thiol:internal standard:pyridine:benzene was 1:1:1:1:25. Analyses by glc were made at various time intervals over a total period of 45 minutes. During this time, the solutions were standing at room temperature. The concentrations of the olefin and the thiol showed a steady decrease in the solution containing pyridine. Those concentrations were essentially constant in the solution containing no pyridine.

Procedure for Determining the Relative Reactivities of Substituted α-Methylstyrenes towards Thiophenol

A competitive method was used to determine the relative reactivities of the substituted α-methylstyrenes. The reference olefin was p-chloro-α-methylstyrene. Its reactivity is the one to which all other olefins would be initially compared. This choice was made in order to simplify the glc analysis. Solutions were prepared containing a substituted α-methylstyrene, p-chloro-α-methylstyrene, thiophenol, o-dichlorobenzene, and benzene in the approximate mole ratio 1:1:1:1:5.6. These solutions were then divided up among eight

glass ampoules. The ampoules were frozen in a dry-ice/isopropanol mixture, evacuated, flushed with nitrogen, allowed to thaw, and this process repeated several times. After the final evacuation, the tubes were sealed. One tube was retained as a control. The others were placed in an oil bath, the temperature of which was maintained at a constant 70.0°C. Photolytic initiation was provided by a 275-watt sunlamp. After the reaction was over, the reacted tubes were kept frozen in a dry ice/isopropanol bath until they could be analyzed. Analysis consisted of injecting several aliquots from the control tube and one from each of the reacted tubes into the gas-liquid chromatograph. The areas under the peaks corresponding to each of the two olefins, thiophenol, and o-dichlorobenzene were thus determined both before and after the reaction.

With this data, there are two possible ways to calculate the rate ratio. The direct method involves determining the relative amounts of disappearance of the two olefins. The other is an indirect calculation in which the changes in the peak areas of one of the olefins and the thiophenol are monitored.

The first step in either of the calculations is to calculate the areas of the olefins and thiophenol relative to the area of the internal standard.

$$X = \frac{A}{S} \qquad \text{(Eq. 50)}$$

X is a relative area, A is the actual measurement of area, and S

is the area of the internal standard. In the direct method, then, the

rate ratio is given by

$$\text{Rate Ratio } \left(\frac{\text{Olefin 1}}{\text{Olefin 2}}\right) = \frac{R_1}{R_2} = \frac{\ln\left(\frac{x_1^i}{x_1^f}\right)}{\ln\left(\frac{x_2^i}{x_2^f}\right)} \qquad \text{(Eq. 51)}$$

where the subscripts refer to the olefins and the superscripts i and f

refer to unreacted and reacted samples, respectively.

In the indirect method, the denominator corresponding to a

standard olefin is calculated in the same manner as above. The

numerator is calculated as follows:

$$\frac{x_1^i}{x_1^f} = \frac{M_1}{M_1 - M_s \left(1 - \frac{x_s^f}{x_s^i}\right) + M_2 \left(1 - \frac{x_2^f}{x_2^i}\right)} \qquad \text{(Eq. 52)}$$

where the M's are the number of moles of each of the indicated

species as were weighed out in the initial preparation of the reaction

mixture and the subscripts again refer to olefins 1 and 2 and to thio-

phenol (S). The denominator of this expression (Eq. 52) calculates

the amount of olefin 1 left after reaction by subtracting from the

initial moles of olefin 1 the total moles of thiophenol that have

reacted and then adding back the number of those moles of thiophenol

that disappeared by reaction with olefin 2.

In the case of substituted α-methylstyrenes, the relative rates

were determined relative to p-chloro-α-methylstyrene. Since it

was desired to relate the reactivites to that of the unsubstituted

compound, the following conversion was carried out

$$\frac{R_x}{R_H} = \left(\frac{R_x}{R_{f-Cl}}\right)\left(\frac{R_{f-Cl}}{R_H}\right)$$
(Eq. 53)

The data for the addition of thiophenol to substituted α-methyl-

styrenes is presented in Tables 14-21 in the appendix.

Procedure for Determining the Relative Reactivities of Substituted Thiophenols towards p-Chloro-α-methylstyrene

These kinetics experiments were run in exactly the same way

as above, the ratio of substituted thiophenol: thiophenol: p-chloro-

α-methylstyrene: o-dichlorobenzene: benzene being 1:1:1:1:5.6.

Again photoinitiation was used and the temperature was 70.0°C.

The data are shown in Tables 22-25 in the appendix.

Procedure for Determining the Relative Reactivities
of Isopropenylarenes towards Thiophenol

The ratio for this series of compounds was 1:1:1:1:10 for iso-propenylarene: 2-isopropenylnaphthalene: thiophenol: o-dichloro-benzene: benzene. To determine the reactivity of α-methylstyrene to 2-isopropenylnaphthalene, the actual kinetics experiment involved p-chloro-α-methylstyrene versus 2-isopropenylnaphthalene for reasons of glc separation. The reactivity of the p-chloro compound from the first study was then used to calculate the relative reactivity of α-methylstyrene in this study.

It was found that photolysis was not necessary for initiation since there were sufficient peroxide impurities in the reagents to provide an adequate rate of radical formation. Everything else was the same as above.

The results are shown in Tables 26-29 of the appendix.

Procedure for Determining the Relative Reactivities
of Vinylarenes towards Thiophenol

Several changes in procedure were necessary in order to study this series of compounds. As the reference olefin, p-methoxy-α-methylstyrene was chosen. Also, the low solubility of some of these compounds necessitated more dilute solutions. The ratio of

vinylarene: p-methoxy-α-methylstyrene: thiophenol: o-dichloro-benzene: benzene was typically 1:1:1:1:75, although the amount of benzene varied considerably. Finally, two different methods of initiation were required since the thermal method used earlier was not effective in the dilute solutions here employed. Photolysis was used as in the case of the substituted α-methylstyrenes, except for the anthracene and pyrene derivatives which apparently underwent photolytic reactions. In those situations, a small amount of benzoyl peroxide was introduced into each of the ampoules that was to be reacted.

In all cases, the indirect method of analysis had to be employed, since many of the vinylarenes seemed to be prone to polymerization under glc conditions.

See Tables 31-38 in the appendix for the data.

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APPENDICES

Table 14. Relative rate of disappearance of $\underline{p}$-methoxy-α-methylstyrene to $\underline{p}$-chloro-α-methylstyrene

Conditions: 45 minutes at 70°C.

Mmoles $C_6H_4Cl_2$: 4.899

Mmoles C_6H_6:   28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	$R_{\underline{p}-CH_3O}/R_{\underline{p}-Cl}$
1	$\underline{p}$-CH$_3$O	4.922	1.822	3.100	62.99	1.42[a]
	$\underline{p}$-Cl	4.913	2.435	2.478	50.36	
	PhSH	5.188	0.207	4.981	98.01	1.01[b,c]
2	$\underline{p}$-CH$_3$O	4.922	1.783	3.139	63.78	1.92
	$\underline{p}$-Cl	4.913	2.894	2.021	41.03	
	PhSH	5.188	0.244	4.944	95.30	1.70
3	$\underline{p}$-CH$_3$O	4.922	1.814	3.108	63.14	1.81
	$\underline{p}$Cl	4.913	2.828	2.085	42.34	
	PhSH	5.188	0.346	4.842	93.33	1.49
4	$\underline{p}$-CH$_3$O	4.922	1.830	3.092	62.81	1.93
	$\underline{p}$Cl	4.913	2.938	1.975	40.08	
	PhSH	5.188	0.523	4.665	89.92	1.54
5	$\underline{p}$-CH$_3$O	4.922	1.924	3.008	61.12	1.82
	$\underline{p}$-Cl	4.913	2.913	2.000	40.52	
	PhSH	5.188	0.647	4.541	87.53	1.39
6	$\underline{p}$-CH$_3$O	4.922	1.968	2.954	60.01	1.99
	$\underline{p}$-Cl	4.913	3.092	1.821	36.94	
	PhSH	5.188	0.843	4.345	83.75	1.55
7	$\underline{p}$-CH$_3$O	4.922	1.903	3.019	61.34	1.89
	$\underline{p}$-Cl	4.913	2.969	1.944	39.46	
	PhSH	5.188	0.609	4.529	88.26	1.52

Average[a] $R_{\underline{p}-CH_3O}/R_{\underline{p}-Cl} = 1.89 \pm 0.05$ Average[b] $R_{\underline{p}-CH_3O}/R_{\underline{p}-Cl} = 1.53 \pm 0.08$

a) Direct method   b) Indirect method   c) Not included in average

Table 15. Relative rate of disappearance of p, α-dimethylstyrene to p-chloro- α-methylstyrene

Conditions: 75 minutes at 70°C.

Mmoles $C_6H_4Cl_2$: 4.816

Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{p-CH_3}/R_{p-Cl}
1	p-CH$_3$	5.031	3.072	1.959	38.93	1.48[a]
	p-Cl	5.001	3.582	1.419	28.30	
	PhSH	4.983	1.321	3.662	73.49	1.73[b]
2	p-CH$_3$	5.031	2.897	2.134	42.42	1.40
	p-Cl	5.001	3.365	1.636	32.64	
	PhSH	4.983	1.060	3.923	78.73	1.53
3	p-CH$_3$	5.031	2.634	2.397	47.64	1.65
	p-Cl	5.001	3.374	1.627	32.45	
	PhSH	4.983	0.527	4.456	87.42	2.10
4	p-CH$_3$	5.031	2.503	2.528	50.25	1.42
	p-Cl	5.001	3.061	1.940	38.74	
	PhSH	4.983	0.095	4.888	98.09	1.78
5	p-CH$_3$	5.031	3.120	1.911	37.99	1.19
	p-Cl	5.001	3.338	1.663	33.14	
	PhSH	4.983	1.176	3.807	76.40	1.37
6	p-CH$_3$	5.031	2.554	2.477	49.24	1.21
	PhSH	4.983	0.028	4.955	99.44	1.45

Average[a] R_{p-CH_3}/R_{p-Cl} = 1.39 ± 0.13   Average[b] R_{p-CH_3}/R_{p-Cl} = 1.66 ± 0.21

a) Direct method   b) Indirect method

Table 16. Relative rate of disappearance of $\underline{m},\alpha$ -dimethylstyrene to $\underline{p}$-chloro-α -methylstyrene

Conditions: 50 minutes at 70°C.

Mmoles $C_6H_4Cl_2$:   4.574

Mmoles C_6H_6:   28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	$R_{\underline{m}\text{-}CH_3}/R_{\underline{p}\text{-}Cl}$
1	$\underline{m}$-CH$_3$	4.924	2.453	2.471	50.18	1.11[a]
	$\underline{p}$-Cl	4.869	2.597	2.272	46.55	
	PhSH	5.062	0.144	4.918	97.16	1.23[b]
2	$\underline{m}$-CH$_3$	4.924	2.424	2.500	50.78	1.21
	$\underline{p}$-Cl	4.869	2.699	2.170	44.44	
	PhSH	5.062	0.187	4.875	96.31	1.58
3	$\underline{m}$-CH$_3$	4.924	2.619	2.305	46.81	1.26
	$\underline{p}$-Cl	4.869	2.944	1.925	39.42	
	PhSH	5.062	0.236	4.826	95.34	1.51
4	$\underline{m}$-CH$_3$	4.924	2.393	2.531	51.41	1.21
	$\underline{p}$-Cl	4.869	2.675	2.194	44.94	
	PhSH	5.062	0.191	4.871	96.23	1.31
5	$\underline{m}$-CH$_3$	4.924	2.340	2.584	52.48	1.12
	$\underline{p}$-Cl	4.869	2.501	2.368	48.54	
	PhSH	5.062	0	5.062	100.00	1.19
6	$\underline{m}$-CH$_3$	4.924	2.474	2.450	49.76	1.18
	$\underline{p}$-Cl	4.869	2.707	2.162	44.31	
	PhSH	5.062	0.114	4.948	97.75	1.42
7	$\underline{m}$-CH$_3$	4.924	2.112	2.812	57.10	1.15
	$\underline{p}$-Cl	4.869	2.333	2.536	51.98	
	PhSH	5.062	0.140	4.922	97.23	0.90

Average[a] $R_{\underline{m}\text{-}CH_3}/R_{\underline{p}\text{-}Cl} = 1.18 \pm 0.04$ Average[b] $R_{\underline{m}\text{-}CH_3}/R_{\underline{p}\text{-}Cl} = 1.31 \pm 0.17$

a) Direct method   b) Indirect method

Table 17. Relative rate of disappearance of p-chloro-α-methylstyrene to α-methylstyrene

Conditions: 60 minutes at 70°C.

Mmoles C_6H_5Cl: 5.075

Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{p-Cl}/R_H
1	p-Cl	4.793	2.496	2.297	47.93	0.99[a]
	H	5.097	2.778	2.301	48.38	
	PhSH	5.358	0.440	4.918	91.79	0.90[b]
2	p-Cl	4.793	2.900	1.893	39.49	0.81
	H	5.079	3.182	2.897	46.04	
	PhSH	5.358	0.449	4.909	91.62	0.56[c]
3	p-Cl	4.793	2.778	2.015	42.04	0.94
	H	5.079	3.060	2.019	44.10	
	PhSH	5.358	0.533	4.825	90.05	0.68
4	p-Cl	4.793	2.870	1.923	40.12	0.91
	H	5.079	3.151	1.928	43.08	
	PhSH	5.358	0.765	4.593	85.72	0.69
5	p-Cl	4.793	2.820	1.973	41.47	1.00
	H	5.079	3.100	1.979	41.17	
	PhSH	5.358	0.562	4.796	89.51	0.69
6	p-Cl	4.793	2.909	1.884	39.30	0.95
	H	5.079	3.191	1.888	40.86	
	PhSH	5.358	0.992	4.366	81.49	0.75
7	p-Cl	4.793	2.883	1.910	39.86	1.06
	H	5.079	3.165	1.914	38.03	
	PhSH	5.358	1.029	4.329	80.80	0.79

Average[a] $R_{p-Cl}/R_H = 0.74 \pm 0.12$ Average[b] $R_{p-Cl}/R_H = 0.74 \pm 0.12$

a) Direct method   b) Indirect method   c) Not included in average

Table 18. Relative rate of disappearance of m-methoxy- α-methylstyrene to p-chloro- α-methylstyrene

Conditions: 53 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 4.743
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{m-CH_3O}/R_{p-Cl}
1	m-CH$_3$	4.937	2.498	2.439	49.40	1.05[a]
	p-Cl	5.572	2.910	2.662	47.70	
	PhSH	5.045	0.426	4.619	91.56	0.78[b]
2	m-CH$_3$O	4.937	2.497	2.440	49.42	1.06
	p-Cl	5.572	2.925	2.647	47.43	
	PhSH	5.045	0.488	4.557	90.33	0.76
3	m-CH$_3$O	4.937	2.514	2.423	49.08	1.05
	p-Cl	5.572	2.916	2.656	47.54	
	PhSH	5.045	0.444	4.601	91.20	0.77
4	m-CH$_3$O	4.937	2.299	2.638	53.44	1.10
	p-Cl	5.572	2.769	2.803	50.24	
	PhSH	5.045	0.352	4.693	93.00	0.69
5	m-CH$_3$O	4.937	2.503	2.407	48.75	1.02
	p-Cl	5.572	2.887	2.685	48.12	
	PhSH	5.045	0.326	4.719	93.54	0.81
6	m-CH$_3$O	4.937	2.601	2.336	47.32	1.05
	p-Cl	5.572	3.027	2.545	45.61	
	PhSH	5.045	0.208	4.837	95.88	1.92[b]
7	m-CH$_3$O	4.937	2.683	2.254	45.65	1.04
	p-Cl	5.572	3.090	2.482	44.46	
	PhSH	5.045	0.459	4.586	90.90	0.94

Average[a] $R_{m-CH_3O}/R_{p-Cl} = 1.05 \pm 0.02$ Average[b] $R_{m-CH_3O}/R_{p-Cl} = 0.82 \pm 0.09$

a) Direct method   b) Indirect method

Table 19. Relative rate of disappearance of m-trifluoromethyl- α -methylstyrene to p-chloro-α -methylstyrene

Conditions: 90 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 5.259
Mmoles C_6H_6:   28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{m-CF_3}/R_{p-Cl}
1	m-CF$_3$	4.994	3.224	1.770	35.44	0.60[a]
	p-Cl	5.154	2.465	2.689	52.01	
	PhSH	4.894	0.360	4.534	92.64	0.63[b]
2	m-CF$_3$	4.994	3.218	1.776	35.56	0.65
	p-Cl	5.154	2.612	2.542	49.15	
	PhSH	4.894	0.464	4.430	90.52	0.69
3	m-CF$_3$	4.994	3.232	1.762	35.28	0.63
	p-Cl	5.154	2.564	2.590	50.09	
	PhSH	4.894	0.440	4.344	88.76	0.62
4	m-CF$_3$	4.994	3.712	1.282	25.68	0.55
	p-Cl	5.154	3.005	2.149	41.52	
	PhSH	4.984	0.739	4.155	84.90	0.95
5	m-CF$_3$	4.994	3.493	1.501	30.06	0.53
	p-Cl	5.154	2.627		48.87	
	PhSH	4.894	0.694	4.200	85.82	0.61
6	m-CF$_3$	4.994	3.190	1.804	36.12	0.68
	p-Cl	5.154	2.658	2.496	48.28	
	PhSH	4.894	0.394	4.520	92.36	0.78
7	m-CF$_3$	4.994	3.590	1.404	28.12	0.54
	p-Cl	5.154	2.793	2.361	45.64	
	PhSH	4.894	0.658	4.236	86.55	0.77

Average[a] $R_{m-CF_3}/R_{p-Cl} = 0.60 \pm 0.05$ Average[b] $R_{m-CF_3}/R_{p-Cl} = 0.68 \pm 0.06$

a) Direct method   b) Indirect method

Table 20.   Relative rate of disappearance of m-trifluoromethyl- α-methylstyrene to m-chloro-α-methylstyrene

Conditions: 95 minutes at 70°C.

Mmoles $C_6H_4Cl_2$:   4.850
Mmoles C_6H_6:   28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{m-CF_3}/R_{m-Cl}
1	$m-CF_3$	5.006	3.491	1.515	30.26	0.86[a]
	$m-Cl$	4.961	3.272	1.689	34.19	
	PhSH	4.684	0.354	4.330	92.44	1.80[b,c]
2	$m-CF_3$	5.006	3.338	1.668	33.32	0.82
	$m-Cl$	4.961	3.012	1.949	39.06	
	PhSH	4.684	0.501	4.183	89.30	1.18
3	$m-CF_3$	5.006	3.418	1.588	31.72	0.89
	$m-Cl$	4.961	3.152	1.809	36.64	
	PhSH	4.684	0.638	4.046	86.38	1.30
4	$m-CF_3$	5.006	3.413	1.593	31.82	0.82
	$m-Cl$	4.961	3.116	1.845	37.36	
	PhSH	4.684	0.730	3.954	84.42	1.18
5	$m-CF_3$	5.006	3.482	1.524	30.44	0.88
	$m-Cl$	4.961	3.290	1.671	33.87	
	PhSH	4.684	0.808	3.786	82.75	1.41
6	$m-CF_3$	5.006	3.422	1.584	31.64	0.83
	$m-Cl$	4.961	3.152	1.809	36.64	
	PhSH	4.684	0.938	3.746	79.79	1.08
7	$m-CF_3$	5.006	3.197	1.809	36.13	1.01
	$m-Cl$	4.961	3.184	1.777	35.96	
	PhSH	4.684	1.017	3.667	78.29	1.07

Average[a] R_{m-CF_3}/R_{m-Cl} = 0.84 ± 0.02   Average[b] R_{m-CF_3}/R_{m-Cl} = 1.20 ± 0.10

a) Direct method   b) Indirect method   c) Not included in average

Table 21. Relative rate of disappearance of p-nitro-α-methylstyrene to p-chloro-α-methylstyrene

Conditions: 75 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 4.612
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{p-NO_2}/R_{p-Cl}
1	p-NO$_2$	4.778	3.252	1.526	31.93	1.01[a]
	p-Cl	4.862	3.395	1.467	31.57	
	PhSH	4.250	1.581	2.669	62.80	0.81[b]
2	p-NO$_2$	4.778	2.744	2.034	42.56	1.28[c]
	p-Cl	4.862	3.213	1.649	35.25	
	PhSH	4.250	1.527	2.723	64.07	0.61
3	p-NO$_2$	4.778	3.210	1.568	32.81	1.14
	p-Cl	4.862	3.495	1.367	29.56	
	PhSH	4.250	1.979	2.271	53.44	0.64
4	p-NO$_2$	4.778	3.437	1.341	28.06	0.94
	p-Cl	4.862	3.493	1.369	29.58	
	PhSH	4.250	1.685	2.565	60.35	0.87
5	p-NO$_2$	4.778	3.332	1.446	30.27	0.99
	p-Cl	4.862	3.448	1.414	30.50	
	PhSH	4.250	1.663	2.587	60.87	0.82
6	p-NO$_2$	4.778	3.574	1.204	25.20	0.94
	p-Cl	4.862	3.642	1.220	26.57	
	PhSH	4.250	1.826	2.424	57.04	1.01
7	p-NO$_2$	4.778	3.334	1.444	30.23	1.09
	p-Cl	4.862	3.567	1.295	28.08	
	PhSH	4.250	2.084	2.166	50.96	0.65

Average[a] R_{p-NO_2}/R_{p-Cl} = 1.02 ± 0.06   Average[b] R_{p-NO_2}/R_{p-Cl} = 0.77 ± 0.18

a) Direct method   b) Indirect method   c) Not included in average

Table 22. Relative rate of disappearance of p-methoxythiophenol to thiophenol

Conditions: 35 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 4.497
Mmoles C_6H_6:   28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	$R_{p\text{-}CH_3O}/R_H$
1	p-CH₃O	4.973	2.683	2.290	46.05	1.69
	H	4.777	3.317	1.460	30.56	
	Olefin	5.018	0.431	4.587	91.41	
2	p-CH₃O	4.973	2.714	2.259	45.43	1.61
	H	4.777	3.278	1.499	31.38	
	Olefin	5.018	0.455	4.563	90.93	
3	p-CH₃O	4.973	2.565	2.408	48.82	1.80
	H	4.777	2.921	1.865	38.85	
	Olefin	5.018	0.564	4.454	88.76	
4	p-CH₃O	4.973	2.815	2.158	43.40	1.50
	H	4.777	3.273	1.540	31.48	
	Olefin	5.018	0.416	4.602	91.71	
5	p-CH₃O	4.973	2.611	2.362	47.49	1.72
	H	4.777	3.286	1.491	31.22	
	Olefin	5.018	0.380	4.638	92.42	
6	p-CH₃O	4.973	2.722	2.251	45.26	1.56
	H	4.777	3.243	1.534	32.11	
	Olefin	5.018	0.651	4.367	87.03	

Average $R_{p\text{-}CH_3O}/R_H = 1.65 \pm 0.09$

Table 23. Relative rate of disappearance of p-methylthiophenol to thiophenol

Conditions: 45 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 4.396
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{p-CH_3}/R_H
1	p-CH$_3$	4.898	3.120	1.778	36.31	0.96
	H	5.170	3.235	1.935	37.42	
	Olefin	4.878	0.062	4.816	98.72	
2	p-CH$_3$	4.898	3.248	1.650	33.69	0.97
	H	5.170	3.390	1.780	32.42	
	Olefin	4.878	0.096	4.782	98.04	
3	p-CH$_3$	4.898	3.182	1.716	35.04	1.04
	H	5.170	3.411	1.759	34.03	
	Olefin	4.878	0.107	4.771	97.80	
4	p-CH$_3$	4.898	3.355	1.543	31.51	1.00
	H	5.170	3.542	1.628	31.49	
	Olefin	4.878	0.063	4.815	98.72	
5	p-CH$_3$	4.898	2.897	2.001	40.86	1.00
	H	5.170	3.049	2.121	41.02	
	Olefin	4.878	0.098	4.780	98.00	
6	p-CH$_3$	4.898	3.104	1.794	36.62	1.02
	H	4.170	3.292	1.878	36.32	
	Olefin	4.878	0.112	4.766	97.70	
7	p-CH$_3$	4.898	3.177	1.721	35.13	1.04
	H	5.170	3.410	1.760	34.04	
	Olefin	4.878	0.109	4.769	97.76	

Average $R_{p-CH_3}/R_H = 1.00 \pm 0.02$

Table 24. Relative rate of disappearance of p-chlorothiophenol to thiophenol

Conditions: 40 minutes at 70°C
Mmoles $C_6H_4Cl_2$: 4.787
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{p-Cl}/R_H
1	p-Cl	5.028	3.773	1.255	24.96	0.87
	H	4.933	3.542	1.391	28.20	
	Olefin	4.897	0.272	4.625	94.45	
2	p-Cl	5.028	3.721	1.307	25.99	0.88
	H	4.933	3.501	1.432	29.03	
	Olefin	4.897	0.340	4.497	91.84	
3	p-Cl	5.128	3.808	1.220	24.26	0.78
	H	4.933	3.449	1.484	30.08	
	Olefin	4.897	0.354	4.543	92.77	
4	p-Cl	5.028	3.980	1.048	20.84	0.74
	H	4.933	3.597	1.336	27.08	
	Olefin	4.897	0.363	4.534	92.58	
5	p-Cl	5.028	3.480	1.548	30.79	1.03
	H	4.933	3.449	1.484	30.09	
	Olefin	4.897	0.684	4.212	86.01	
6	p-Cl	5.028	3.652	1.376	27.37	0.94
	H	4.933	3.511	14.22	28.83	
	Olefin	4.897	0.547	4.350	88.83	

Average R_{p-Cl}/R_H = 0.87 ±0.08

Table 25. Relative rate of disappearance of p-nitrothiophenol to thiophenol

Conditions: 50 minutes at 70 °C.
Mmoles $C_6H_4Cl_2$: 4.925
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{p-NO_2}/R_H
1	$p-NO_2$	4.457	2.796	1.661	37.26	0.69
	H	5.026	2.567	2.459	48.92	
	Olefin	4.927	1.295	3.632	73.71	
2	$p-NO_2$	4.457	2.977	1.480	33.21	0.63
	H	5.026	2.652	2.374	47.24	
	Olefin	4.927	1.922	3.005	61.00	
3	$p-NO_2$	4.457	3.097	1.360	30.51	0.59
	H	5.026	2.721	2.305	45.87	
	Olefin	4.927	1.320	3.607	73.20	
4	$p-NO_2$	4.457	3.265	1.192	26.74	0.50
	H	5.026	2.697	2.328	46.32	
	Olefin	4.927	1.102	3.825	77.63	
5	$p-NO_2$	4.457	3.041	1.416	31.76	0.65
	H	5.026	2.784	2.242	44.61	
	Olefin	4.927	1.542	3.385	68.70	
6	$p-NO_2$	4.457	3.361	1.096	24.58	0.49
	H	5.026	2.833	2.193	43.63	
	Olefin	4.927	1.864	3.063	62.17	

Average $R_{p-NO_2}/R_H = 0.59 \pm 0.06$

Table 26. Relative rate of disappearance of 2-isopropenylnaphthalene to p-chloro-α-methylstyrene

Conditions: 30 minutes at 70°C.

Mmoles $C_6H_4Cl_2$: 1.759
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{2-N}/R_{p-Cl}
1	2-N	2.864	1.531	1.333	46.56	1.53
	p-Cl	3.162	2.100	1.062	33.59	
	PhSH	3.307	0.583	2.724	82.37	
2	2-N	2.864	1.588	1.276	44.57	1.54
	p-Cl	3.162	2.153	1.009	31.91	
	PhSH	3.307	0.742	2.565	77.55	
3	2-N	2.864	1.523	1.341	46.83	1.60
	p-Cl	3.162	2.132	1.030	32.59	
	PhSH	3.307	0.694	2.613	79.01	
4	2-N	2.864	1.480	1.384	48.34	1.56
	p-Cl	3.162	2.059	1.103	34.87	
	PhSH	3.307	0.658	2.649	80.11	
5	2-N	2.864	1.380	1.484	51.80	1.59
	p-Cl	3.162	2.000	1.162	36.74	
	PhSH	3.307	0.593	2.714	82.08	
6	2-N	2.864	1.594	1.270	44.33	1.59
	p-Cl	3.162	2.189	0.973	30.76	
	PhSH	3.307	0.751	2.556	77.29	

Average $R_{2-N}/R_{p-Cl} = 1.57 \pm 0.03$

Table 27. Relative rate of disappearance of 1-isopropenylnaphthalene to 2-isopropenylnaphthalene

Conditions: 30 minutes at 70°C.

Mmoles: $C_6H_4Cl_2$: 2.779
Mmoles: C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{1-N}/R_{2-N}
1	1-N	2.973	2.686	0.287	9.65	0.082
	2-N	2.810	0.820	1.990	70.81	
	PhSH	2.953	0.742	2.211	74.86	
2	1-N	2.973	2.611	0.362	12.16	0.091
	2-N	2.810	0.671	2.139	76.11	
	PhSH	2.953	0.483	2.470	83.65	
3	1-N	2.973	2.658	0.315	10.61	0.093
	2-N	2.810	0.838	1.972	70.17	
	PhSH	2.953	0.582	2.371	80.29	
4	1-N	2.973	2.743	0.230	7.47	0.113
	2-N	2.810	1.381	1.429	50.85	
	PhSH	2.953	0.644	2.309	78.19	

Average $R_{1-N}/R_2\text{-}N = 0.095 \pm 0.009$

Table 28. Relative rate of disappearance of 9-isopropenylanthracene to 1-isopropenylnaphthalene

Conditions: 420 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 2.068
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{9-A}/R_{1-N}
1	9-A	1.693	1.563	0.130	7.68	0.39
	1-N	2.505	2.043	0.462	18.46	
	PhSH	2.668	1.901	0.767	28.77	
2	9-A	1.693	1.681	0.012	0.705	0.043
	1-N	2.505	2.128	0.377	15.03	
	PhSH	2.668	2.106	0.562	21.06	
3	9-A	1.693	1.620	0.073	4.34	0.20
	1-N	2.505	1.999	0.506	20.19	
	PhSH	2.668	2.038	0.630	23.61	
4	9-A	1.693	1.671	0.022	1.29	0.059
	1-N	2.505	2.011	0.494	19.74	
	PhSH	2.668	2.098	0.570	21.35	

Average R_{9-A}/R_{1-N} = 0.17 ±0.12

Table 29. Relative rate of disappearance of 9-isopropenylphenanthrene to 2-isopropenylnaphthalene

Conditions: 30 minutes at 70°C
Mmoles $C_6H_4Cl_2$: 1.758
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{9-P}/R_{2-N}
1	9-P	2.517	2.384	0.133	5.30	0.026
	2-N	2.882	0.358	2.524	87.58	
	PhSH	3.012	0.099	2.913	96.71	
2	9-P	2.517	2.264	0.253	10.06	0.045
	2-N	2.882	0.273	2.609	90.54	
	PhSH	3.012	0.144	2.868	95.22	
3	9-P	2.517	2.362	0.155	6.16	0.032
	2-N	2.882	0.393	2.489	86.38	
	PhSH	3.012	0.418	2.594	86.12	
4	9-P	2.517	2.375	0.142	5.65	0.028
	2-N	2.882	0.360	2.522	87.52	
	PhSH	3.012	0.342	2.670	88.63	

Average R_{9-P}/R_{2-N} = 0.033 ± 0.006

Table 30. Relative rate of disappearance of styrene to p-methoxy-α-methylstyrene

Conditions: 10 hours 20 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 0.4469
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_s/R_{p-CH_3O}
1	S	0.5144	0.2363	0.2781	54.06	0.89
	p-CH$_3$O	0.5151	0.2159	0.2992	58.09	
	PhSH	0.5773	0	0.5773	100.00	
2	S	0.5144	0.2301	0.2843	55.27	0.96
	p-CH$_3$O	0.5751	0.2221	0.2930	56.88	
	PhSH	0.5773	0	0.5773	100.00	
3	S	0.5144	0.2729	0.2415	46.95	0.60
	p-CH$_3$O	0.5151	0.1793	0.3358	65.19	
	PhSH	0.5773	0	0.5773	100.00	
4	S	0.5144	0.2548	0.2596	50.47	0.73
	p-CH$_3$O	0.5151	0.1974	0.3177	61.68	
	PhSH	0.5773	0	0.5773	100.00	
5	S	0.5144	0.2196	0.2948	57.37	1.07
	p-CH$_3$O	0.5151	0.2326	0.2825	54.84	
	PhSH	0.5773	0	0.5773	100.00	
6	S	0.5144	0.2222	0.2922	56.80	1.04
	p-CH$_3$O	0.5151	0.2300	0.2851	55.35	
	PhSH	0.5773	0	0.5773	100.00	
7	S	0.5144	0.2209	0.2935	57.06	1.04
	p-CH$_3$O	0.5151	0.2313	0.2838	55.10	
	PhSH	0.5773	0	0.5773	100.00	

Average $R_s/R_{p-CH_3O} = 0.91 \pm 0.14$

Table 31. Relative rate of disappearance of 1-vinylnaphthalene to p-methoxy-α-methylstyrene

Conditions: 11 hours 50 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 0.4701
Mmoles C_6H_6: 28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{1-N}/R_{p-CH_3O}
1	1-N	0.5634	0.1454	0.4189	74.23	4.10
	p-CH$_3$O	0.5130	0.3646	0.1484	28.93	
	PhSH	0.5673	0	0.5673	100.00	
2	1-N	0.5643	0.1420	0.4223	74.84	4.2
	p-CH$_3$O	0.5130	0.3680	0.1450	28.27	
	PhSH	0.5673	0	0.5673	100.00	
3	1-N	0.5643	0.1620	0.4023	71.29	3.2
	p-CH$_3$O	0.5130	0.3480	0.1650	32.16	
	PhSH	0.5673	0	0.5673	100.00	
4	1-N	0.5643	0.1613	0.4030	71.42	3.2
	p-CH$_3$O	0.5130	0.3487	0.1643	32.03	
	PhSH	0.5673	0	0.5673	100.00	
5	1-N	0.1443	0.1404	0.4239	75.12	4.2
	p-CH$_3$O	0.5130	0.3696	0.1434	27.95	
	PhSH	0.5673	0	0.5673	100.00	
6	1-N	0.5643	0.1586	0.4057	71.89	3.4
	p-CH$_3$O	0.5130	0.3514	0.1616	31.50	
	PhSH	0.5673	0	0.5673	100.00	
7	1-N	0.5643	0.1689	0.3954	70.07	3.0
	p-CH$_3$O	0.5130	0.3411	0.1719	33.51	
	PhSH	0.5673	0	0.5673	100.00	

Average R_{1-N}/R_{p-CH_3O} = 3.6±0.5

Table 32. Relative rate of disappearance of 2-vinylnaphthalene to p-methoxy-α-methylstyrene

Conditions: 11 hours 15 minutes at 70°C.

Mmoles $C_6H_4Cl_2$: 0.9483
Mmoles C_6H_6: 56.28

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{2-N}/R_{p-CH_3O}
1	2-N	0.9909	0.3303	0.6606	66.67	2.2
	p-CH$_3$O	1.025	0.625	0.400	39.02	
	PhSH	1.061	0	1.061	100.00	
2	2-N	0.9909	0.2880	0.7029	70.94	2.9
	p-CH$_3$O	1.025	0.667	0.358	34.93	
	PhSH	1.061	0	1.061	100.00	
3	2-N	0.9909	0.3194	0.6715	67.77	2.4
	p-CH$_3$O	1.025	0.636	0.289	37.95	
	PhSH	1.061	0	1.061	100.00	
4	2-N	0.9909	0.3119	0.6790	68.52	2.5
	p-CH$_3$O	1.025	0.643	0.382	37.72	
	PhSH	1.061	0	1.061	100.00	
5	2-N	0.9909	0.3512	0.6397	64.56	2.0
	p-CH$_3$O	1.025	0.604	0.421	41.07	
	PhSH	1.061	0	1.061	100.00	
6	2-N	0.9909	0.2761	0.7148	72.14	3.1
	p-CH$_3$O	1.025	0.679	0.346	33.76	
	PhSH	1.061	0	1.061	100.00	
7	2-N	0.9909	0.3218	0.6691	67.52	2.3
	p-CH$_3$O	1.025	0.633	0.392	38.24	
	PhSH	1.061	0	1.060	100.00	

Average R_{2-N}/R_{p-CH_3O} = 2.5 ± 0.3

Table 33. Relative rate of disappearance of 1-vinylanthracene to p-methoxy-α-methylstyrene

Conditions: 19 hours at 70°C.

Mmoles $C_6H_4Cl_2$: 0.4918
Mmoles C_6H_6: 28.14
Mmoles Benzoyl Peroxide: 0.00124

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	$R_{1-A}/R_{p\text{-}CH_3O}$
1	1-A	0.5147	0.2816	0.2331	45.29	5.6
	p-CH_3O	0.6918	0.6210	0.0708	10.23	
	PhSH	0.5100	0.2061	0.3039	59.59	
2	1-A	0.5147	0.3026	0.2121	41.21	7.0
	p-CH_3O	0.6918	0.6411	0.0507	7.33	
	PhSH	0.5100	0.2472	0.2628	51.35	
3	1-A	0.5147	0.2761	0.2386	0.46.36	5.8
	p-CH_3O	0.6918	0.6216	0.0702	10.15	
	PhSH	0.5700	0.2012	0.3088	60.55	
4	1-A	0.5147	0.2821	0.2326	45.19	4.4
	p-CH_3O	0.6918	0.6031	0.0887	12.82	
	PhSH	0.5100	0.1887	0.3212	63.00	
5	1-A	0.5147	0.3128	0.2019	39.23	3.5
	p-CH_3O	0.6918	0.6115	0.0913	13.20	
	PhSH	0.5100	0.2168	0.2932	57.49	

Table 33. Continued.

Conditions: 24 hours 30 minutes at 70°C.
Mmoles $C_6H_4Cl_2$: 0.4197
Mmoles C_6H_6: 28.14
Mmoles Benzoyl Peroxide: 0.00227

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	$R_{1-A}/R_{\underline{p}-CH_3O}$
6	1-A	0.4534	0.1104	0.3430	75.65	8.4
	$\underline{p}$-CH$_3$O	0.7925	0.6699	0.1226	15.47	
	PhSH	0.5309	0.0653	0.4656	87.70	
7	1-A	0.4534	0.1318	0.3216	70.93	8.8
	$\underline{p}$-CH$_3$O	0.7925	0.6891	0.1034	13.05	
	PhSH	0.5309	0.1059	0.4250	80.05	
8	1-A	0.4534	0.1717	0.2817	62.13	5.6
	$\underline{p}$-CH$_3$O	0.7925	0.6676	0.1249	15.76	
	PhSH	0.5309	0.1243	0.4066	76.59	
9	1-A	0.4534	0.1881	0.2653	58.51	3.4
	$\underline{p}$-CH$_3$O	0.6134	0.1791	22.60		
	PhSH	0.5309	0.0865	0.4444	83.71	
10	1-A	0.4534	0.1288	0.3246	71.59	4.2
	$\underline{p}$-CH$_3$O	0.7925	0.5892	0.2033	25.65	
	PhSH	0.5309	0.0030	0.5279	99.43	
11	1-A	0.4534	0.1286	0.3248	71.64	7.3
	$\underline{p}$-CH$_3$O	0.7925	0.6676	0.1249	15.76	
	PhSH	0.5309	0.0812	0.4497	84.71	

Average $R_{1-A}/R_{\underline{p}-CH_3O}$ = 5.9 ±1.5

Table 34. Relative rate of disappearance of 2-vinylanthracene to p-methoxy-α-methylstyrene

Conditions: 23 hours at 70°C.

Mmoles $C_6H_4Cl_2$ 0.3966
Mmoles C_6H_6:   67.54
Mmoles Benzoyl peroxide: 0.00244

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{2-A}/R_{p-CH_3O}
1	2-A	0.5064	0.2608	0.2456	48.50	4.8
	p-CH$_3$O	0.5240	0.4557	0.0683	13.03	
	PhSH	0.5600	0.2461	0.3139	56.05	
2	2-A	0.5064	0.2454	0.4610	51.54	7.8
	p-CH$_3$O	0.5240	0.4772	0.468	8.93	
	PhSH	0.5600	0.2522	0.3078	54.96	
3	2-A	0.5064	0.2534	0.2530	49.96	4.0
	p-CH$_3$(	0.5240	0.4414	0.0826	15.76	
	PhSH	0.5600	0.2244	0.3356	59.93	
4	2-A	0.5064	0.2452	0.2612	51.58	5.2
	p-CH$_3$O	0.5340	0.4560	0.0680	12.98	
	PhSH	0.5600	0.2308	0.3292	58.79	

Average R_{2-A}/R_{p-CH_3O} = 5.4 ±1.2

Table 35. Relative rate of disappearance of 9-vinylanthrancene to p-methoxy-α-methylstyrene

Conditions: 18 hours 10 minutes at 70°C.

Mmoles $C_6H_4Cl_2$: 0.7857
Mmoles C_6H_6: 112.56
Mmoles benzoyl peroxide: 0.0351

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{9-A}/R_{p-CH_3O}
1	9-A	0.8348	0.7280	0.1068	12.79	2.7
	p-CH$_3$O	0.9007	0.8562	0.0445	4.94	
	PhSH	1.011	0.860	0.151	14.94	
2	9-A	0.8348	0.8169	0.0179	2.14	0.4
	p-CH$_3$O	0.9007	0.8546	0.0461	5.12	
	PhSH	1.011	0.947	0.064	6.33	
3	9-A	0.8348	0.7383	0.0965	11.56	0.8
	p-CH$_3$O	0.9007	0.7825	0.1182	13.12	
	PhSH	1.011	0.7963	0.2147	21.24	
4	9-A	0.8348	0.7462	0.0886	10.61	3.2
	p-CH$_3$O	0.9007	0.8702	0.0305	3.39	
	PhSH	1.011	89.19	0.1191	11.78	
5	9-A	0.8348	0.7126	0.1222	14.64	3.2
	p-CH$_3$O	0.9007	0.8570	0.0437	4.85	
	PhSH	1.011	0.8451	0.1659	16.41	
6	9-A	0.8348	0.7698	0.0650	7.79	0.7
	p-CH$_3$O	0.9007	0.8056	0.0951	10.56	
	PhSH	1.011	0.8509	0.1601	15.84	

Average R_{9-A}/R_{p-CH_3O} = 1.6 ± 1.2

Table 36.   Relative rate of disappearance of 9-vinylphenanthrene to p-methoxy-α-methylstyrene

Conditions: 12 hours 35 minutes at 70°C.
Mmoles $C_6H_4Cl_2$:   1.022
Mmoles C_6H_6:   28.14

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{9-Ph}/R_{p-CH_3O}
1	9-Ph	0.5956	0.2455	0.3501	58.78	1.4
	p-CH$_3$O	0.5212	0.2710	0.2502	48.00	
	PhSH	0.6209	0.0206	0.6003	96.68	
2	9-Ph	0.5956	0.2221	0.3735	62.71	1.9
	p-CH$_3$O	0.5212	0.3077	0.2135	40.96	
	PhSH	0.6209	0.0339	0.5870	94.54	
3	9-Ph	0.5956	0.2040	0.3916	65.75	2.0
	p-CH$_3$O	0.5212	0.3077	0.2135	40.96	
	PhSH	0.6209	0.0158	0.6051	97.45	
4	9-Ph	0.5956	0.2415	0.3541	59.45	1.6
	p-CH$_3$O	0.5212	0.2966	0.2246	43.09	
	PhSH	0.6209	0.0422	0.5787	93.20	
5	9-Ph	0.5956	0.2360	0.3596	60.38	1.7
	p-CH$_3$O	0.5212	0.3009	0.2203	42.27	
	PhSH	0.6209	0.0410	0.5799	93.40	
6	9-Ph	0.5956	0.2185	0.3771	63.31	1.9
	p-CH$_3$O	0.5212	0.306	0.2152	41.29	
	PhSH	0.6209	0.0286	0.5923	95.39	
7	9-Ph	0.5959	0.2262	0.3694	62.02	1.8
	p-CH$_3$O	0.5212	0.3018	0.2194	42.10	
	PhSH	0.62.09	0.0321	5.888	94.83	

Average $R_{9-Ph}/R_{p-CH_3O} = 1.8 \pm 0.2$

Table 37. Relative rate of disappearance of 1-vinylpyrene to p-methoxy-α-methylstyrene

Conditions: 19 hours 30 minutes at 70°C.

Mmoles $C_6H_4Cl_2$: 0.4408
Mmoles C_6H_6: 28.14
Mmoles benzoyl peroxide: 0.00198

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{1-py}/R_{p-CH_3O}
1	1-py	0.4711	0.1722	0.2989	63.45	17.4
	p-CH$_3$O	0.5212	0.4922	0.0290	5.56	
	PhSH	0.4509	0.1230	0.3279	72.72	
2	1-py	0.4711	0.2047	0.2664	56.55	10.2
	p-CH$_3$O	0.5212	0.4804	0.0408	7.83	
	PhSH	0.4509	0.1437	0.3072	68.13	
3	1-py	0.4711	0.1568	0.3143	66.72	14.8
	p-CH$_3$O	0.5212	0.4839	0.0373	7.16	
	PhSH	0.4509	0.0993	0.3516	77.98	
4	1-py	0.4711	0.1969	0.2742	58.20	7.0
	p-CH$_3$O	0.5212	0.4600	0.0612	11.74	
	PhSH	0.4509	0.1155	0.3354	74.38	
5	1-py	0.4711	0.2571	0.2140	45.43	6.8
	p-CH$_3$O	0.5212	0.4764	0.0448	8.60	
	PhSH	0.4509	0.1921	0.2588	57.40	
6	1-py	0.4711	0.2251	0.2460	52.22	5.7
	p-CH$_3$O	0.5212	0.4576	0.0636	12.20	
	PhSH	0.4509	0.1413	0.3096	68.66	
7	1-py	0.4711	0.1751	0.2960	62.83	11.5
	p-CH$_3$O	0.5212	0.4782	0.0430	8.25	
	PhSH	0.4509	0.1119	0.3390	75.18	

Average $R_{1-py}/R_{p-CH_3O} = 10.5 \pm 3.5$

Table 38. Relative rate of disappearance of 6-vinylchrysene to p-methoxy-α-methylstyrene

Conditions: 11 hours 55 minutes at 70°C.

Mmoles $C_6H_4Cl_2$:   0.4190
Mmoles C_6H_6:   39.40

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	% Rxn	R_{6-C}/R_{p-CH_3O}
1	6-C	0.4827	0.1322	0.3503	72.61	4.1
	p-CH_3O	0.5212	0.3799	0.1413	27.11	
	PhSH	0.4918	0	0.4918	100.00	
2	6-C	0.4827	0.1453	0.3374	69.90	3.4
	p-CH_3O	0.5212	0.3668	0.1544	29.62	
	PhSH	0.4918	0	0.4918	100.00	
3	6-C	0.4827	0.1484	0.3343	69.26	3.3
	p-CH_3O	0.5212	0.3637	0.1575	30.22	
	PhSH	0.4918	0	0.4918	100.00	
4	6-C	0.4872	0.1463	0.3364	69.69	3.4
	p-CH_3O	0.5212	0.3658	0.1554	29.82	
	PhSH	0.4918	0	0.4918	100.00	
5	6-C	0.4827	0.1387	0.3440	71.27	3.7
	p-CH_3O	0.5212	0.3734	0.1478	28.36	
	PnSH	0.4918	0	0.4918	100.00	
6	6-C	0.4827	0.1662	0.3165	65.57	3.1
	p-CH_3O	0.5212	0.3459	0.1753	33.63	
	PnSH	0.4918	0	0.4918	100.00	
7	6-C	0.4827	0.1425	0.3402	70.48	3.6
	p-CH_3O	0.5212	0.3459	0.1753	33.63	
	PnSH	0.4918	0	0.4918	100.00	

Average R_{6-C}/R_{p-CH_3O} = 3.5±0.2