AN ABSTRACT OF THE THESIS OF

GARY SCOTT NOLAN for the degree of MASTER OF SCIENCE

in CHEMISTRY presented on June 6, 1979

Title: SUBSTITUENT EFFECTS IN HYDROGEN ABSTRACTION BY TRICHLOROMETHYL RADICAL FROM 10-SUBSTITUTED-9-METHYLANTHRACENES; A LINEAR FREE ENERGY STUDY

Abstract approved: Redacted for Privacy

Dr. Gerald Jay Gleicher

Hydrogen abstraction by the trichloromethyl radical from a series of 10-substituted-9-methylanthracenes at 70° has been examined. The logarithms of the relative rates, measured against hydrogen abstraction from fluorene, correlate very well with sigma plus parameters within the Hammett formalism. A rho value of -0.78 ± 0.05 was observed with a correlation constant of .99 and a standard regression from the mean of .06. This result implies a charge separated character to the transition state with stabilization by electron donating groups. The present work serves as a rigorous test of "Pryor's Postulate". That statement holds that the reaction constant or rho value for aryl methyl hydrogen abstraction is, within experimental uncertainties, the same as that for aromatic substitution into the nonmethylated arene. Since a substitution study within the Hammett framework has already been performed, the present

study makes a comparison of rho values possible. The rho value obtained in the trichloromethylation of 9-substituted-anthracenes at 70° was -0.83 ± 0.04. This agrees well with the present result. This agreement tends to substantiate and extend "Pryor's Postulate" by treating relatively selective radicals and polycyclic systems.

Substituent Effects in Hydrogen Abstraction by Trichloromethyl Radical from 10-substituted-9-methylanthracenes; A Linear Free Energy Study

by

Gary Scott Nolan

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1980

APPROVED:

Redacted for Privacy

Associate Professor of Chemistry

in charge of major

Redacted for Privacy

Acting Head of Department of Chemistry

Redacted for Privacy

Dean of Graduate School

Date thesis is presented June 6, 1979

Typed by Clover Redfern for Gary Scott Nolan

ACKNOWLEDGMENTS

The author would like to express gratitude to Dr. Gerald Jay Gleicher not only for the ideas that resulted in this project but also for his appreciation of problems both personal and scientific. In addition, thanks are due to Dr. Bruce Schatz and Robert Cordova for their assistance in materials preparation. Finally, the author wishes to convey indebtedness to his wife, Laura, for her kind perserverence.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

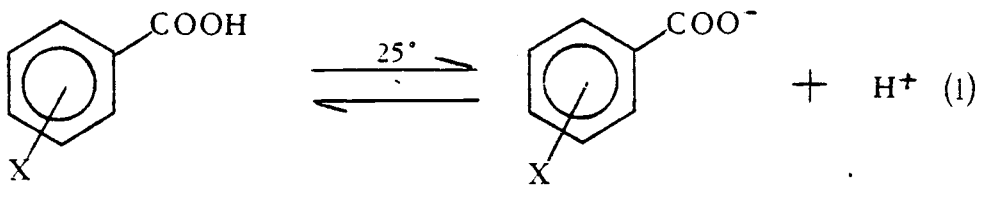
SUBSTITUENT EFFECTS IN HYDROGEN ABSTRACTION BY TRICHLOROMETHYL RADICAL FROM 10-SUBSTITUTED-9-METHYLANTHRACENES; A LINEAR FREE ENERGY STUDY

I. INTRODUCTION

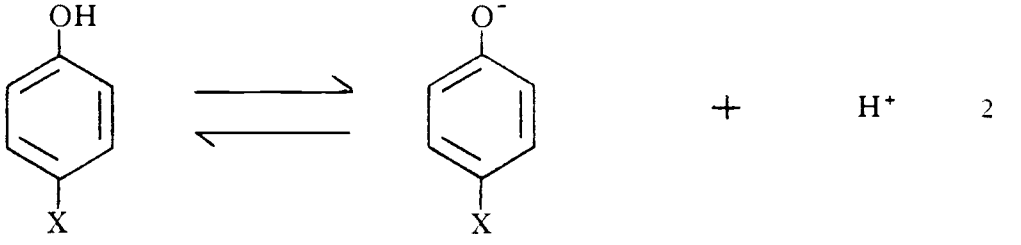
The well known two parameter Hammett linear free energy equation:

$$\log K/K_0 = \sigma\rho \quad \sim \text{or} \sim \quad \log k/k_0 = \sigma\rho$$

was originally elaborated as a means of correlating rates or equilibria of organic ionic reactions (1). Since that time it has also demonstrated its utility in treating radical processes which may be defined as those reactions in which bond breaking is homolytic in character (2). The paradigm of activation or linear free energy differences along some reaction coordinate as a function of aromatic substituents has led to variations on the earlier Hammett theme. In the original study, the value of rho, the reaction constant in the linear free energy equation, was set at unity for the following reaction (Eq. 1):

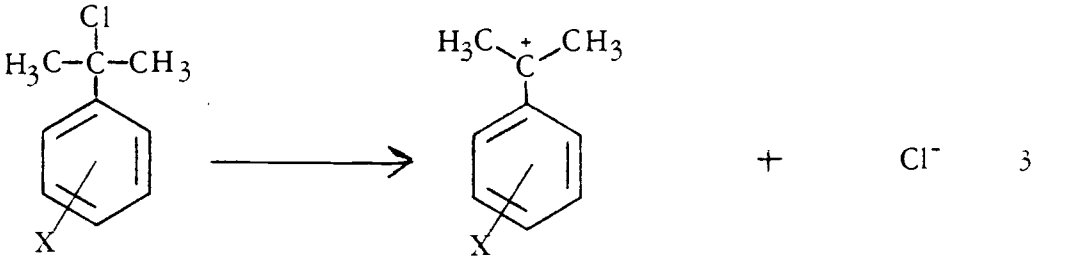


The equilibrium constants were measured for each particular substituent X in the <u>meta</u> (σ_m) and <u>para</u> (σ_p) positions, K_0 refers to the ionization constant of the parent benzoic acid system. The σ values or structural factors thus obtained allow the determination of other rho values and hence sensitivity factors for other various reactions. While the original substituent parameters are useful for systems resembling benzoic acid, for other reactions the correlations break down. This occurs when the charge at the reaction site is capable of a direct mesomeric interaction with the substituent (Eq. 2):



2

This was noted for certain cases involving generation of negative charge (Eq. 2) by Hammett himself (1). The corresponding situation for positive charge development (Eq. 3) was examined by Brown some 20 years later (3):

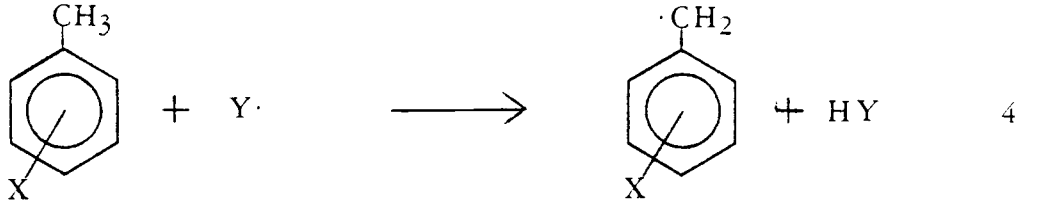


3

Different substituent parameters can thus be developed. The above solvolysis reaction defines the sigma plus (σ^+) parameters with a rho value of -4.54 on scale with the earlier benzoic acid system. This avenue of parameter development has proven to be particularly fruitful.

Many types of free radical reactions can be shown to occur with rates amenable to linear free energy correlations. These processes include, among others, examples of addition (4a), halogen abstraction (4b), and perester (4c) and peroxide decompositions (4d). A more detailed discussion of two radical processes, namely hydrogen abstraction and aromatic substitution follows below.

With respect to hydrogen abstraction, the comparatively small energetic differences among substituted toluenes are best elucidated via attack by selective radicals as generalized in equation 4:



4

Highly reactive abstracting agents generally tend to be less satisfactory due to a leveling out or masking of the potential substrate and substituent dependence. The magnitude of the reaction constant rho reflects the selectivity in radical attack while the sign of rho provides

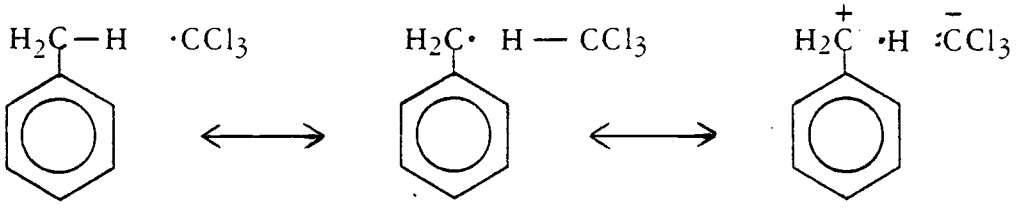
a general indication of the electrophilic or nucleophilic nature of the attacking species. Table I summarizes the rho values and the type of substituent constant associated with typical attacking radicals. Although certain qualitative selectivity trends can be observed among the entries, caution must be observed in making comparisons due to temperature and solvent variations among the species employed.

Table I. Hydrogen abstraction reaction constants and substituent parameters.

Y·	ρ	σ/σ^+	T (°C)	Ref
Cl_3C	-1.24	σ^+	50	5a
Br	-1.39	σ^+	80	5b, c
Cl	-0.4	σ	40	5d
tBuO	-0.4	σ^+	40	5e
C_6H_5	-0.1	σ	60	5f
H_3C	~0	σ	100	5g
H	-0.1	σ	40	5h
$C_{10}H_{19}CH_2$	+0.49	σ	80	5i, j
$(CH_3)_3C$	+0.99	σ	30	5k

The question of which substituent constant provides optimum correlation has been associated with the concept of a polar or charge separated transition state whose character is somewhere between homolytic and heterolytic bond cleavage (6). Viewed in terms of the traditional resonance hybrid, the transition state for hydrogen abstraction by a typically electrophilic trichloromethyl radical may

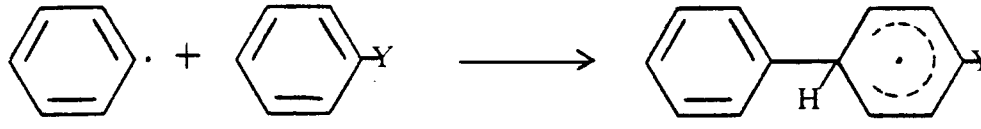
be illustrated as follows:



By maintaining the attacking radical constant, one may also obtain information about the variation of substituents in a series of related substrates. In this fashion, several research groups (7) have noted that substitution of the methyl hydrogens on toluene by alkyl moieties introduces a stabilizing influence on radical development which in turn diminishes the substituent dependence. This is not always true, however, as in instances when destabilizing steric interactions between bulky attacking radicals and alkyl groups may exist. The differences with respect to size are manifest, for example, between the trichloromethyl radical and bromine atom in hydrogen abstraction from cumenes (8) or neopentyl benzenes (9). The larger trichloromethyl radical due to steric reasons will evince a greater aromatic substituent dependence in the aforementioned process. The interplay between alkyl group stabilization, steric factors, and substituent dependencies is reflected in the magnitude of rho and may be treated in a quantitative fashion (10).

Whether the relative rates correlate best with sigma or sigma plus allows some insight as to the nature of the rate determining transition step. Besides the above discussed charge separated contributing forms, optimum linearity with respect to sigma plus implies delocalization of the radical onto the substituent. Correspondingly correlation with the sigma parameter evinces a picture of lessened delocalization at the transition state, with predominantly inductive rather than mesomeric substituent stabilization.

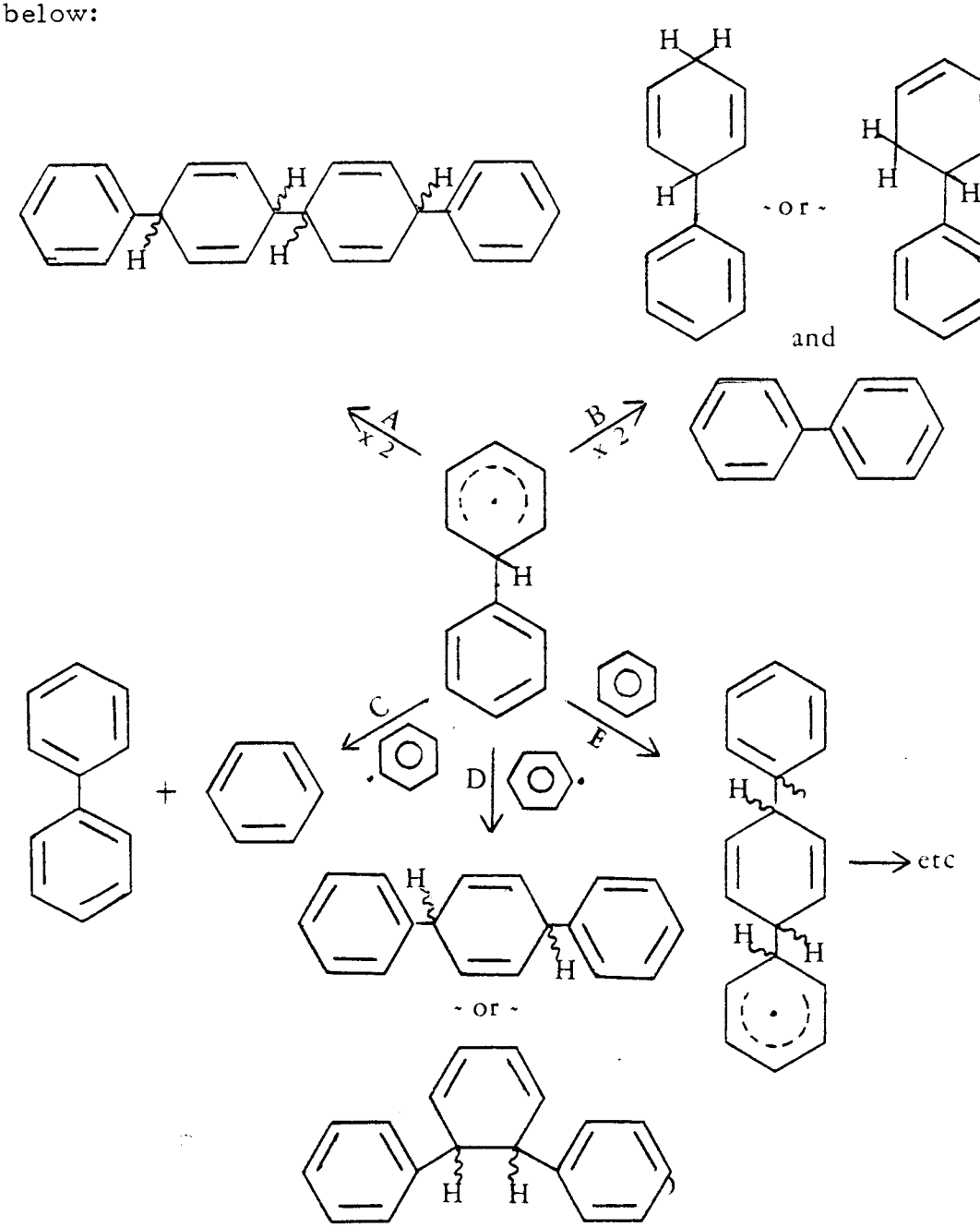
Free radical implication in aromatic substitution reactions was noted by Grieve and Hey in 1934 (11) as a means of interpreting the Gomberg reaction. This reaction involves phenylation of aromatic substrates (Eq. 5):



(5)

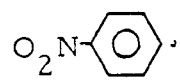
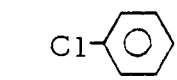
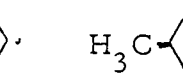
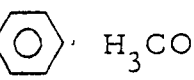
Waters in 1941 (12) showed that the rate determining step was attack by phenyl radical upon the aromatic substrate (Eq. 5). Early efforts argued for a constancy of isomeric product ratios despite variations in the reaction conditions. Unfortunately these results were suspect because of experimental difficulties in separating and identifying the various isomers. Doubt was also cast upon

these quantitative measurements as the role of side reactions were not clearly comprehended. These include dimerization--path A, disproportionation--path B, hydrogen abstraction--path C, radical combination--path D, and polymerization--path E as are illustrated below:



Early efforts directed towards quantitation also utilized the phenyl radical as the attacking species. This was natural as the Gomberg reaction is a useful route to the coupling of aromatic substrates. Prior to any Hammett like formulations, substituent variation in the aryl radical and corresponding influences on relative rates were investigated (13). The following table summarizes subsequent Hammett information gained from some selected phenylation procedures (14):

Table II. Reaction constants for phenylations of substituted benzenes.

Radical					
ρ	-0.81	-0.27	0.05	0.03	0.09

As is apparent, a wide range of selectivities with respect to the attacking radical is observed. Good correlations were noted for attack in the meta position. The deviations for para substituents, however, led the authors to introduce a third parameter to the Hammett equation, τ_p, to account for conjugative effects between the substituent and the nascent radical site.

Reactions utilizing radicals of greater electrophilicity have also been examined within the Hammett scheme. Various oxygen radicals have been thusly investigated. Table III provides some

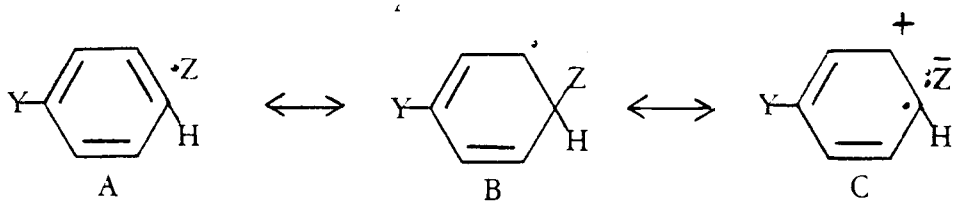
examples of this type of reaction:

Table III. Reaction constants for the attack of oxy-radicals on substituted benzenes.

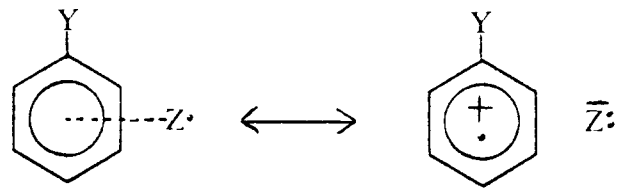
Radical	HO·	H_3C⟨⬡⟩$CO_2^{\cdot}$	⟨⬡⟩$CO_2^{\cdot}$	O_2N⟨⬡⟩$CO_2^{\cdot}$	$H\text{-}C(CH_3)_2\text{-}O\text{-}CO_2^{\cdot}$
ρ	-0.41	-1.28	-1.61	-2.52	~-2.
Ref.	15	16	16	16	17

All the above reactions correlate best with sigma plus substituent constants save that involving the hydroxyl radical. The magnitudes of most of these rho values demonstrate even greater substrate sensitivity than those illustrated in the phenylation reactions. That hydroxyl radical attack correlates better with sigma instead of sigma plus is in line with the earlier observations from hydrogen abstractions where non-selective radicals generally correlated with the sigma constants. The hydroxy radical is comparatively reactive and nonselective.

There are certain models for the transition state of radical aromatic substitution which have been generally deduced from the nature of the Hammett correlations. Where sigma plus correlates the data best, appreciable charge separation is inferred:



Here as in hydrogen abstraction, the positive charge is capable of a mesomeric interaction with the substituent Y. In cases where sigma constants yield the better correlation, a transition state devoid of significant contribution by form C is visualized as the intermediate transient form. Further, a correlation with sigma may imply a rate determining complexation of radical and aromatic substrate (18):



This pi or charge transfer complex affords greater radical selectivity and hence increased substituent dependence. All reactions which are purported to involve rate determining formation of such pi complexes show correlation with sigma rather than sigma plus (19).

A natural extension of the Hammett equation beyond benzene derivatives is to approach the more complex, but essentially comparable, polycyclic aromatics. There are, however, few examples of the application of linear free energy relationships to these

systems where radical processes are concerned. The primary thrust of most radical studies in this area has been the variation of a series of aromatic substrates as opposed to introduction of substituents within the same common polycyclic molecule. This has led to "theoretical" correlations involving energy differences as determined by molecular orbital calculations and their comparisons with relative reactivities for a given reaction.

The earliest examples on radical aromatic substitution by alkyl radicals were studied by Szwarc and coworkers (20). Trichloromethyl radical substitution has also been examined by Kooyman and Farenhorst (21). These endeavors essentially established the basis for choice of aromatic systems and type of molecular orbital computational technique employed.

A second major utilization of molecular orbital theory to correlate radical reactions has been concerned with the generation of 1-arylalkyl type radicals schematically shown in equation 6:

$$\mathrm{ArCHZ} \rightarrow \mathrm{ArC\dot{H}} + \mathrm{Z}\cdot \qquad (6)$$

(with R substituents on the benzylic carbon)

The first such attempt was carried out by Kooyman (22). The results, however, we so disheartening that the problem lay dormant for over 15 years. Unruh and Gleicher (23) later studied the abstraction of benzylic hydrogens from polycyclic, benzenoid

methylarenes (Eq. 7):

$$ArCH_3 + \cdot CCl_3 \longrightarrow Ar\dot{C}H_2 + HCCl_3 \qquad (7)$$

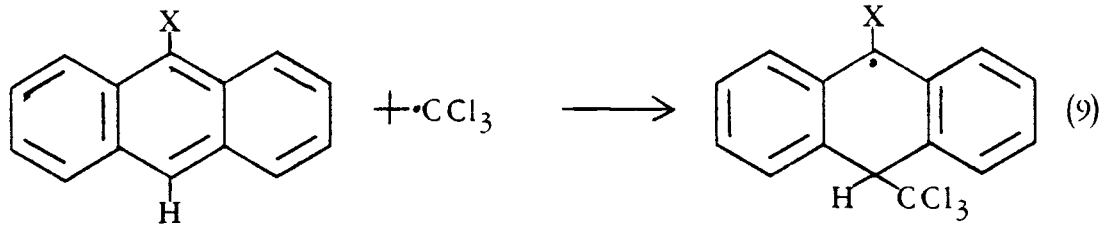
The overall optimum correlation of the relative rates of this reaction with calculated energy differences was excellent ($r = 0.977$) if these increments were ascertained via the more exacting SCF approach. Similar results were later obtained by Church and Gleicher (24) for a radical addition process (Eq. 8):

$$ArCH{=}CH_2 + \cdot S\langle\bigcirc\rangle \longrightarrow Ar\dot{C}HCH_2S\langle\bigcirc\rangle \qquad (8)$$

The above studies are certainly Hammett like if the indicated energy difference calculations possess some relationship to a substituent parameter (sigma, sigma plus, etc.). This has been recognized and tables of "sigma" values for unsubstituted, polycyclic aryl moieties may be found in the literature (25). These values, however, are quite likely of only marginal utility. Generally ascertained from inadequate Huckel type calculations, they frequently include so called "steric corrections" which have been shown to be artifacts of that approach (26).

Within the literature, there exists one example of a "true" Hammett correlation of a radical process in an appropriately substituted polycyclic system. Arnold, Gleicher, and Unruh (27) have

studied the trichloromethylation of 9-substituted anthracenes (Eq. 9):

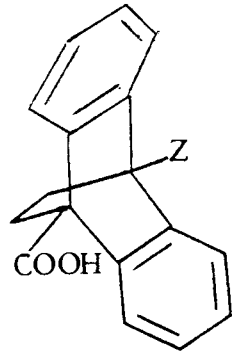


(9)

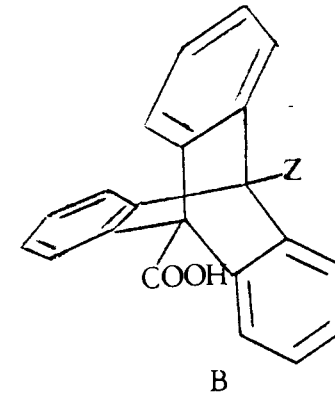
By correlating relative rates of reaction against para sigma plus substituent constants, a correlation coefficient of 0.970 was realized with a reaction constant of -0.83 ± 0.05. The results imply a mesomeric interaction of substituent with the generated radical. The reaction is enhanced by electron donating groups. The specific behavior of certain compounds in the above study may be of additional concern. An increased reactivity, for example, beyond that due to electronic factors alone, was observed for 9-methylanthracene. This was ascribed to hydrogen abstraction from the methyl group. This is a favored route over substitution. Sixty-five percent of the total reaction of this compound occurs via this avenue. Another noteworthy item involves potential 4,5-peri hydrogen interactions with specific substituents leading to consequent inhibition of planarity. Loss of this preferred conformation may preclude significant mesomeric interaction between radical and substituent.

The application of the Hammett equation to polycyclic systems has produced a much more extensive literature in correlating

non-radical processes. Dewar and coworkers (28a) have obtained an approximate correlation between substituent parameters derived from the dissociation constants of substituted 1-naphthoic acids, and carbonyl frequency shifts in esters derived from these same acids. The dissociation constants for various napthoic acids were later demonstrated (28b) to correlate well with substituent chemical shifts obtained from ^{19}F nmr spectra. Further linear free energy relationships have been advanced employing 10-substituted-9-anthroic acids and related systems. In one such study (29) the above mentioned anthroic acid dissociation constants were related to substituents through a Hammett type formalism. This same paper related the dissociation constant data to chemical shifts in 10-substituted-9-fluoroanthracenes. The reaction constant for the acid dissociation was over twice that observed for <u>para</u> substituted benzoic acids. The authors have attributed this large substituent to a pi inductive effect (29). Other experiments, however, indicate a polar or field effect model may adequately account for the substituent influence (30, 31, 32). Hammett studies on the dissociation constants for 4-substituted-dibenzobicyclo[2.2.2]-octa-2,5-diene-1-carboxylic acids (A) and 9-substituted-10-triptoic acids (B) have shown excellent correlations between the ionization constants and substituent constants:



A

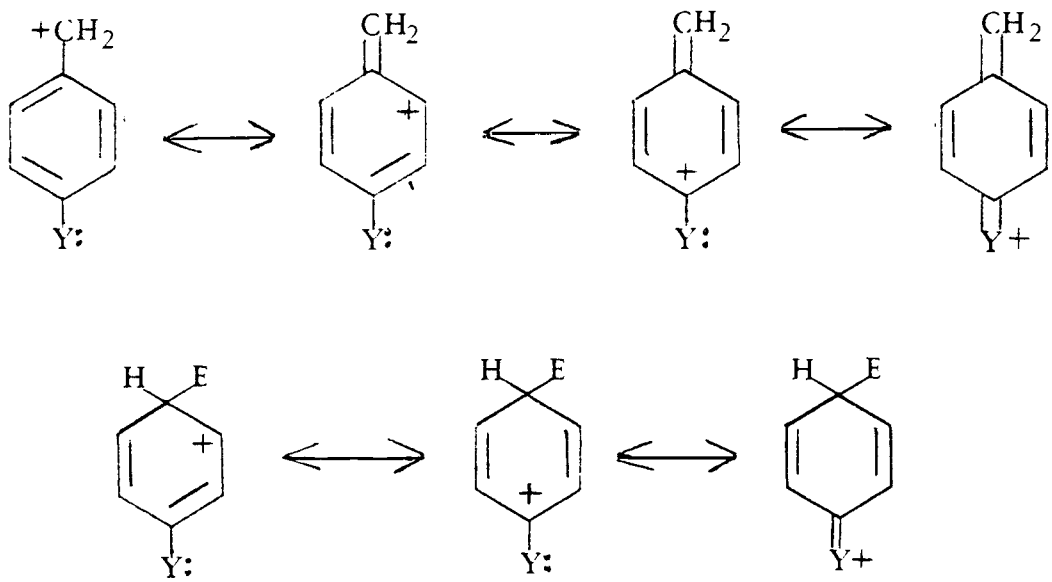


B

The dissociation reactions for all of the above studies done in 50 percent ethanol-water solutions at 25°C reveal equilibrium constants which do not vary to any significant extent. Both the above studies provide a coherent picture of polar substituent effects amenable to linear free energy treatments for higher order aromatic systems and, further, a basis for delineating inductive and mesomeric interactions in these same systems.

II. STATEMENT OF PROBLEM

In benzenoid systems, there exists a decided similarity in Hammett correlations between studies in which the reaction site occurs in conjugation with the ring system and those examples of attack upon the ring itself. This is especially true for electrophilic aromatic substitution at the para position where correlations with sigma plus are obtained. This observation is clarified and rationalized by resonance structures for the respective transition states (33):

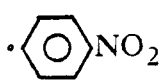
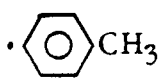
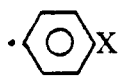


Where radical processes are concerned, the above should at least also be qualitatively true and most pertinent in situations where a higher degree of charge separation is present in the transition state. More explicitly, for selective radical attack, the anticipation

is that of similar sites of charge development for hydrogen abstraction and ring substitution reaction.

Noting the above correspondence in transition state models, Pryor (34) has postulated a quantitative relationship between the respective reactions. He holds that the rho value for hydrogen abstraction by a given radical from substituted toluenes is, within experimental tolerances, identical to that obtained for substitution by the same radical in corresponding benzenes. Supporting experimental data are summarized below:

Table IV. Summary of data leading to Pryor's postulate.

Radical	Hydrogen Abstraction from Toluenes		Substitution in Benzenes	
	ρ	T (°C)	ρ	T (°C)
·H	-0.1	40	-0.2	40
$\cdot CH_3$	-0.2	100	-0.4	85-145
	-0.3	60	-0.3	various
	-0.5	60	-0.4	20
	-0.1	60	-0.4	20
	-0.3[a]	60	-0.2[b]	20

[a] X=Br. [b] X=Cl.

There exist, however, some problems associated with Pryor's experimental input and the strength of his inference. The most compelling shortcoming lies in the fact that few radicals will both abstract hydrogen from a toluene substrate and additionally undergo substitution on a corresponding benzene at the same temperature. More importantly, none of the common, typically electrophilic radicals employed for hydrogen abstraction studies such as chlorine, bromine, trichloromethyl, and tertiary butoxy radicals, etc. will react along a substitution pathway under comparable reaction conditions. Pryor has been obliged to limit his scope mostly to non-selective carbon radicals with relatively low rho values. At this extreme of non-selectivity, comparisons are more tenuous since, as already discussed, energy differences and substituent dependences are swamped. Also, at this extreme the confidence limits associated with schemes such as Pryor's are generally looser and relatively large in comparison with the magnitude of rho.

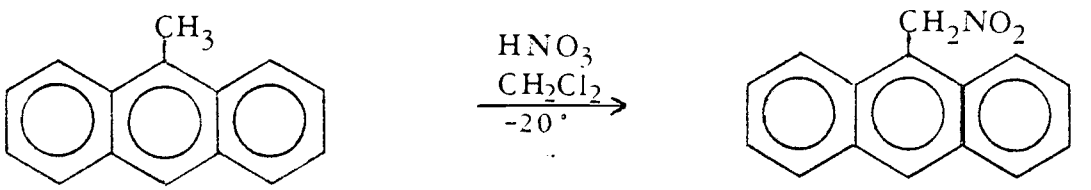
While acknowledging the above limitations, the present work will attempt to circumvent these problems by employing a reaction which should possess a larger rho value. The trichloromethyl radical will be utilized as an abstracting agent. Further, as a means of extending the logic of the linear free energy idea to higher aromatics, the choice of methylanthracenes as substrates affords a comparison where electrophilic substitution and hydrogen abstraction are both

reasonably facile processes. These two processes both occur under the same, easily achievable reaction environments. Since the substitution work has already been performed with a linear free energy relation successfully established (27), there remains only the hydrogen abstraction problem to complete the picture.

III. RESULTS

A. Choice of Substrates

Selection of materials was largely dependent on preserving the comparison with the substitution study (27) on 9-substituted anthracenes. There were, however, certain substrates deemed inappropriate to the planned abstraction study. Alkyl substituents other than methyl were not entertained as possibilities. This was because the various potentially reactive benzylic hydrogens might unduly complicate the proceedings where such abstractions are concerned. The nitro substituent was also omitted. There are no references to 9-methyl-10-nitroanthracene in the literature. Although 9-nitroanthracene, studied in the substitution paper, may be easily prepared by direct nitration of anthracene, that reaction fails for the analogous compound where sidechain nitration is instead observed (35):



At the outset, certain substituents would seem more likely to deviate from any linear relationship. These aberrations might be due to steric interactions with the hydrogen atoms on the 4 and 5 positions

of anthracene peri to the substituent in question. Included among those which would be anticipated as perhaps being "misbehaving" are phenyl, methoxy, and various carbonyl containing groups. All these may show some degree of interaction, in the above mentioned sense, with the nearby hydrogens. Fortunately, methoxy, despite its potential anisotropy, behaves in an ideal fashion (27, 29). This might be a result of the presence of two lone pairs of electrons on the oxygen atom.

Those substrates which would be free of this potential anisotropy would be those monatomic and linear substituents whose minimal size would render this consideration a less important problem. Those would include hydrogen, halogen, and cyano groups. A group like methyl, which by a rotational symmetry yields an invariant steric presence, would also show minimum deviation from the ideal case. Conversely, groups both "bulky" and having anisotropic electronic effects will evince more pronounced peri hydrogen deviations. Most obvious in this regard is the nitro substituent. Evidence from X-ray diffraction (36) and liquid phase (37) studies of 9-nitroanthracene indicates that the steric crowding on the nitro group forces it into an orthogonal orientation relative to the aromatic ring. This is, however, a moot point as 10-nitro-9-methylanthracene is inaccessable. Evidence on 9-phenylanthracene yields a similar overall geometry. The angle between the two rings is somewhere

between 67° (38a) and 70° (38b).

All compounds were synthesized via standard methods, save those commercially available. Certain of the desired substrates were prepared by our collaborators, Bruce Schatz and Robert Cordova, at the College of Idaho. All details are found in the experimental section of this thesis.

B. General Experimental Design

Within our laboratory, the collection of data for relative rate measurements has been satisfactorily realized through gas chromatography, and to a lesser extent, by nuclear magnetic resonance techniques. The former method was felt to be impracticable for the present study. Due to the high molecular weight associated with the anthracene systems, reasonably short retention times required temperatures which could very likely induce pyrolytic reactions on the column. Lower programming temperatures would, on the other hand, result in undesired peak spreading. Despite the higher degree of inherent uncertainty associated with n.m.r. as a quantitative tool, this technique of monitoring the disappearance of methyl protons in the starting materials was employed as the analytical method in the expectation that it ultimately would provide fewer experimental obstacles.

In deciding to use n.m.r. as the analytical device, the question of resolution associated with the choice of reference compound and internal standard became of paramount significance. Diphenylmethane was initially considered as the reference compound. Its relative lack of reactivity, however, led to it being replaced by the more reactive fluorene (39). The latter's reactivity was more in keeping with the range of rates encountered for the various 9-methylanthracenes. As an internal standard, di-tert butylbenzene proved to be ideal. It can be used in small amounts given the large number of equivalent hydrogens whose resonance frequency is well removed from both fluorene and methylanthracene hydrogens, the latter pair being equally well resolved.

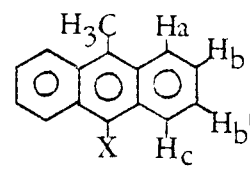
Table V shows nmr data for all the 10-substituted-9-methylanthracenes used in the study. In dissymmetric compounds, two sets of alpha protons, Ha and Hc could usually be delineated, while the protons in the beta sites were unresolvable.

Predominant considerations in establishing reaction conditions involved establishment of a significant extent of reaction and verification that the proper reaction occurred. The temperature was dictated, by the necessity of comparison, to be the same as that maintained in the substitution study.

Thermal radical initiators such as benzoyl peroxide and azoisobutyronitrile required extended reaction times before a notable

amount of reaction could be monitored. In order to circumvent this drawback, photoinitiation was entertained. This method may suffer from a potentially undesired side reaction, namely photodimerization of a ground state molecule with a singlet excited (fluorescing) anthracene molecule (40). While some sort of bandpass filtering seemed to suggest itself, a simpler solution is found in bromobenzene's capacity to act as a singlet quencher (41). This compound was thus employed as a cosolvent with bromotrichloromethane, the source of the photolytically derived radical.

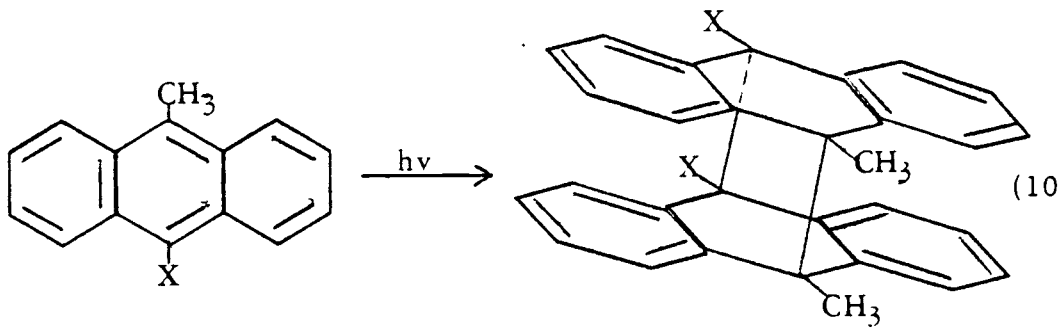
Table V. Proton resonances for the various 10-X-9-methylanthracenes.



X	CH_3	Ha	Hb & Hb'	Hc	Other
$-OCH_3$	2.96	8.16	7.39	8.28	$-OCH_3$ 4.02
$-CH_3$	2.99	8.20	7.38	8.2	
$-C_6H_5$	3.14	8.24		7.41[a]	
-H	2.99	7.91	7.40	8.1	H at C_{10} 8.19
-Cl	3.02	8.16	7.46	8.46	
-Br	3.10	8.26	7.52	8.54	
$-\overset{\overset{O}{\|}}{C}-CH_3$	3.12	7.78	7.44	8.24	CH_3 in acetyl 2.70
$-C\equiv N$	2.94	7.99	7.34	8.38	

[a]Protons Hb, Hb' and those on phenyl substituent inseparable. Multiplet extends from 7.18-7.64, centered as indicated.

While bromobenzene should effectively curtail photodimerization, experiments were nonetheless performed in which dimerization would ostensibly be the favored route (i.e. no bromobenzene or bromotrichloromethane present) (Eq. 10):



(10)

plus other isomer of above dimer

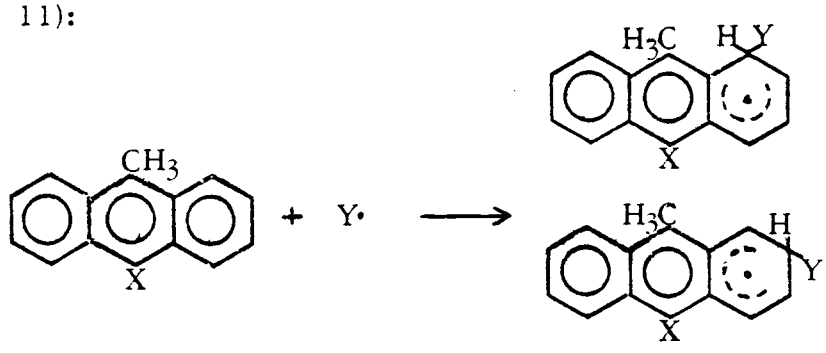
The simple spectrum that arises from the four equivalent methyl groups in the n.m.r. for the dimer of 9, 10-dimethylanthracene made this compound a logical choice. Appearance of the dimer was observed by the increasing presence of the aliphatic (methyl) protons at 2.02 δ and a new aromatic signal at 7.16 δ. As can be seen in the following table, photodimerization in the absence of the quenching agent was a slow process.

Table VI. Extent of dimerization of 9, 10-dimethylanthracene at 80°.

Time (hrs)	24	48	72
% Conversion	4.5	7.4	28.3

It was also observed that the n.m.r. signals noted for photodimer were not present in the spectra of the kinetic trials. Further, the latter experiments were also conducted on a shorter time scale than those required for photodimerization. This small experiment tends to verify the anticipation of dimerization being an unlikely route when substituents block the meso positions. This factor is additionally significant in examining substitution complications below.

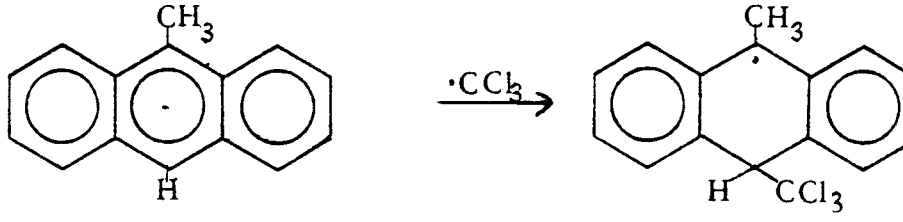
Further side reactions might involve alpha and beta substitution (Eq. 11):



(11)

This manner of radical attack is, happily, not a probable occurrence. Radical substitution of anthracenes is extensively oriented to the meso position (42). Indeed when comparatively reactive, unselective phenyl radicals, generated under conditions of the Meerwein reaction, are allowed to react with anthracene, the isomer distribution is as follows (43): 84% at the 9 position, 14% at 1, and 2% at the 2 site. With one exception, all the molecules studied here have substituents blocking meso attack. Even in the one compound utilized which possesses an unhindered meso position, hydrogen abstraction from the methyl group is still the favored process. Thus it is quite

apparent that methyl hydrogen abstraction is favored. This tendency to attack in the meso position does, however, create a special problem for 9-methylanthracene (Eq. 12).



(12)

A significant amount of reaction will be along this substitution route (27). In order to incorporate this compound within the present correlation, the total extent of reaction was corrected by known relative rates of methyl hydrogen abstraction to substitution.

With respect to evidence for the proper products, peaks at about 5.3 δ were noted in the spectra. These correspond to anthracylbromomethylene protons. The intensities of these absorptions were, however, less than expected for a total accounting of product. Further abstraction of hydrogen from mono and even dibrominated products appears probable to account for a total material balance. In order to examine this conjecture, a regular kinetic run was performed with 10-phenyl-9-chloromethylanthracene reacting in competition with fluorene. Assuming the hypothesis of a polar transition state, chlorine should presumably present at least as stringent test as bromine would. The phenyl substituent itself is only modestly

activating and should be associated with no special effects. Results from this experiment indicated that a second hydrogen abstraction from monohalogenated product is surprisingly facile with the relative rate of reaction of 9-phenyl-10-chloromethylanthracene in comparison to fluorene of 3.52 ± .57. This result can rationalize the apparent lack of material balance. The present result is in keeping with recent data on the relative rates of mono and dibrominations of substituted toluenes (44).

C. Kinetic Results

The preparation of samples utilized about one millimole of fluorene to one half millimole of the anthracene compounds. The only exception was in the case of 10-bromo-9-methylanthracene where only a limited amount of material was available. In order to minimize concentration dependent variations, volumes of bromotrichloromethane and bromobenzene were constant relative to solutes for each kinetic run. Reaction times, temperature, extents of reaction as well as amounts of starting material are all summarized in the Appendix.

All of the tubes were sealed by a common procedure. The solutions were flushed with nitrogen and evacuated while frozen in a dry ice--acetone bath. After several freeze-thaw cycles, the samples were sealed under a reduced pressure of nitrogen.

Temperatures during kinetic runs were controlled to within a tenth of a degree with a constant temperature oil bath.

Table VII summarizes the relative rate data for each of the variously substituted anthracenes as well as the pertinent Hammett sigma parameters.

Table VII. Relative rates of hydrogen abstraction by trichloromethyl radical on 10-substituted-9-methylanthracenes at 70.0°C.

X-Substituent	k_{rel}[a]	log k_{rel}	σ_p^+	σ_p	No. Runs
$-OCH_3$	9.00 ± .52[b]	.05424	-.778	-.268	6
$-CH_3$	4.03 ± .55[c]	.60531	-.311	-.170	7
	1.92 ± .11	.28330	-.179	-.010	5
-H	2.75 ± .32[d]	.43933	0	0	6
-Cl	1.99 ± .29	.29885	.114	.227	5
-Br	1.67 ± .12	.22272	.150	.232	6
$-\overset{\overset{O}{\|\|}}{C}-CH_3$	1.17 ± .18	.06819	.502	.502	6
$-C\equiv N$	.57 ± .03	-.24413	.659	.660	5

[a] relative to fluorene.

[b] average deviation.

[c] statistically corrected.

[d] corrected for ring substitution.

In terms of the correlation, all compounds were well behaved save 10-phenyl-9-methylanthracene which is less reactive than expected. As noted earlier, this possibility was not unanticipated as peri-hydrogen interactions could likely preclude the planarity

presupposed under sigma plus correlations. Table VIII summarizes the results of several Hammett type correlations.

Table VIII. Linear free energy correlations of hydrogen abstraction from 10-substituted-9-methylanthracenes by trichloromethyl radicals.

Sigma Employed	Remarks	Rho	Ave. Dev.	C.C.	S_b
Sigma	all points	-1.05	.09	-.94	.16
Sigma-plus	all points	- .75	.07	-.96	.09
Sigma	excluding phenyl	-1.10	.08	-.97	.12
Sigma-plus	excluding phenyl	- .78	.05	-.99	.06
Sigma-plus	all points, sigma value for phenyl	- .78	.05	-.98	.06

The better correlations were obtained utilizing sigma plus parameters. When all points were treated, a correlation coefficient of .96 was realized as compared to a coefficient of .94 for the sigma correlation. The corresponding slopes were -.75 ± .07 and -1.05 ± .09. The correlation coefficient for the Hammett plot utilizing sigma plus rose to .99 and had a slope of -.78 ± .05 when the phenyl point was omitted. Employing a sigma value for phenyl within a general sigma plus correlation led to a coefficient of .98. A slope of -.78 ± .05 was found. While the ultimate conclusions of this study do not depend upon this sort of latitude in parameter manipulation, an argument might, nonetheless, be advanced wherein a phenyl

substituent is capable of only inductive interactions which are intrinsic to sigma parameters and the mesomeric interplay assumed for sigma plus is precluded by the lack of planarity.

The standard regressions from the mean, which are also given in Table VIII, parallel the correlation coefficients throughout. Graphs illustrating the correlations (excluding phenyl in computing the least squares fit) are shown for sigma in Figure I and for sigma plus in Figure II.

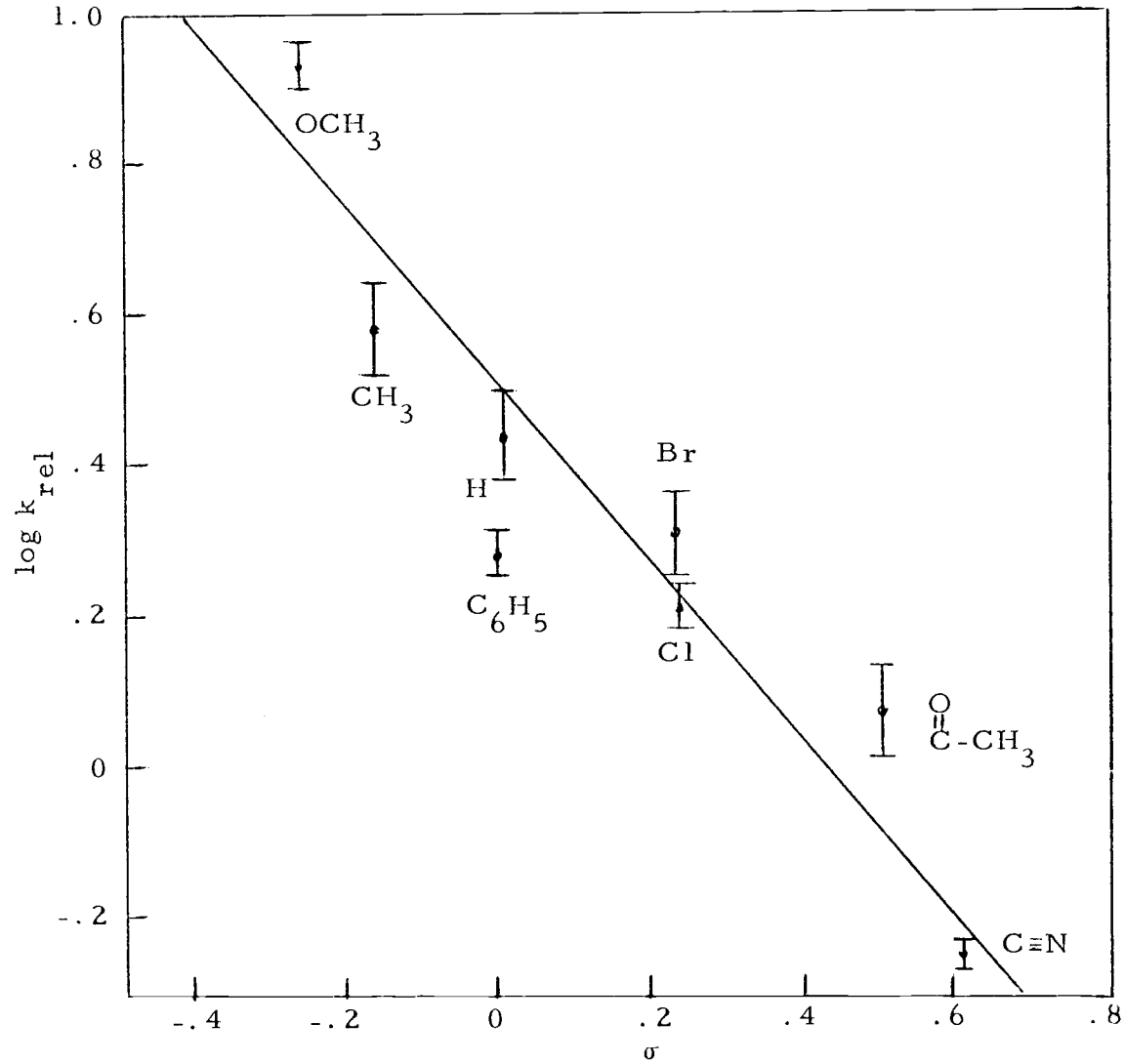


Figure I. Logarithms of the relative rates of hydrogen abstraction versus sigma.

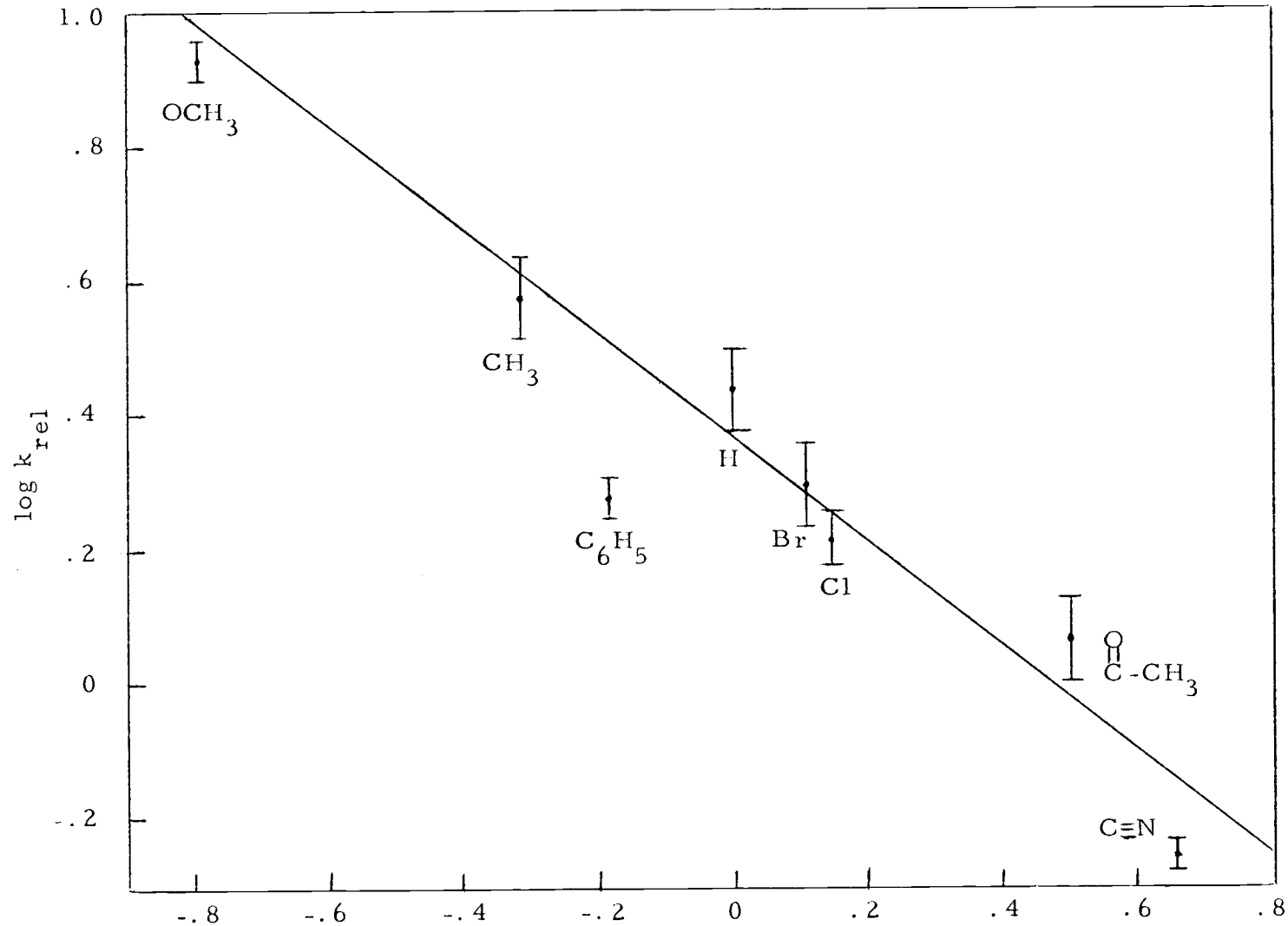


Figure II. Logarithms of the relative rates of hydrogen abstraction versus sigma plus.

IV. DISCUSSION

A comparison of the present results to those of the substitution experiment evince a fair amount of correspondence. The rho values of $-.78 \pm .05$ here and $-.83 \pm .05$ for that of Arnold, et al. are equivalent within experimental error. A graph of the present relative rate data versus that from the substitution study is shown in Figure III. As one might expect, a slope of near unity ($.97 \pm .05$) is seen and concurrently an excellent coefficient of correlation of .98, when omitting phenyl, is obtained.

The above lends apparent experimental support to Pryor's postulate; that is the rho value for hydrogen abstraction from "benzylic" positions on aromatic compounds is essentially the same as that realized from the corresponding ring substitution reactions. This conclusion is seen as a more rigorous test of the above mentioned hypothesis. The trichloromethyl radical, unlike the unselective radical agents cited by Pryor in formulating his idea, exhibits the dual nature of being sufficiently reactive under identical reaction conditions for both hydrogen abstraction and aromatic substitution and yet being a rather selective species.

It is also interesting that Pryor's original benzene-toluene comparison can apparently be extended to higher aromatics (i.e. anthracene and 9-methylanthracene). Self consistent field molecular

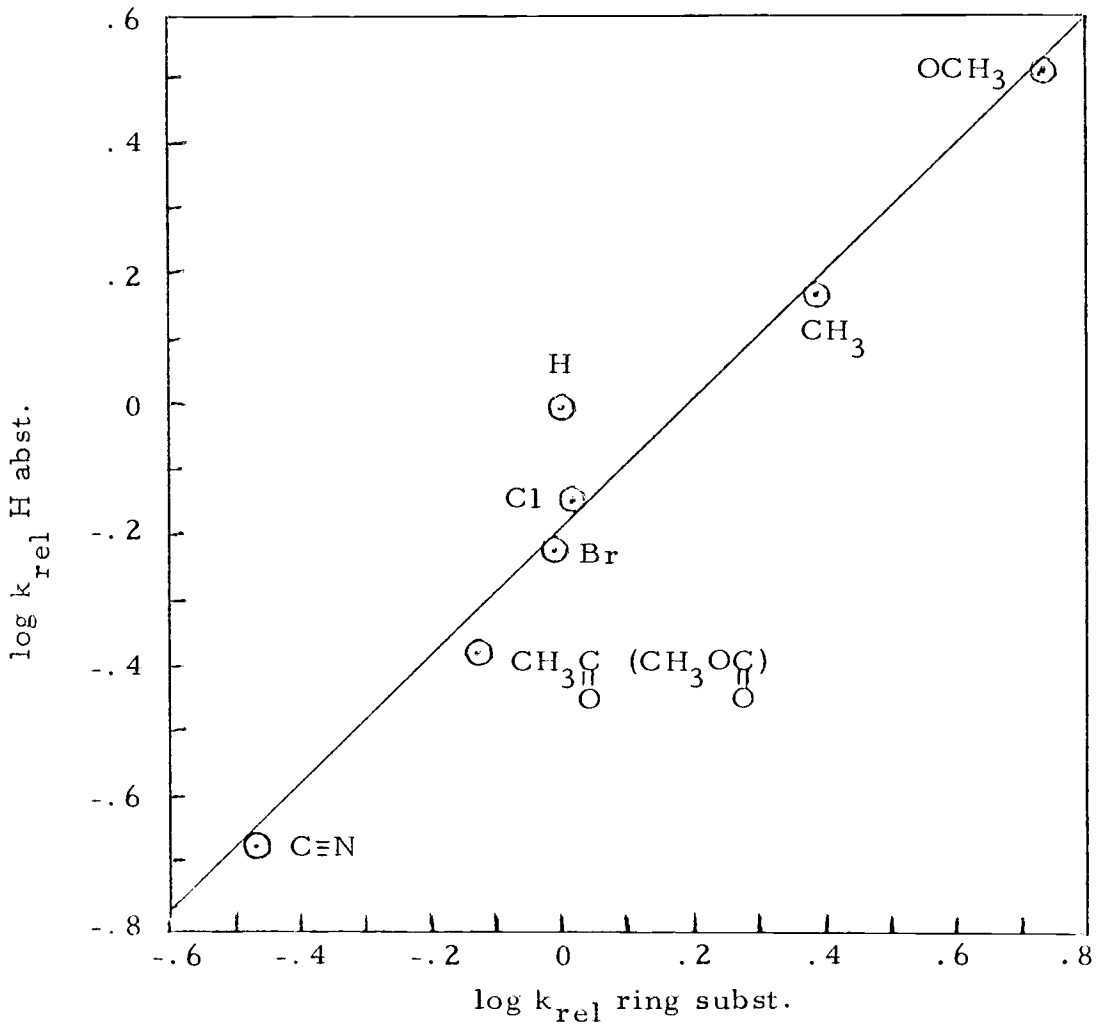


Figure III. Relative rates of hydrogen abstraction versus relative rates of aromatic substitution.

orbital calculations indicate that the energy differences, though close, are not identical for the relative ring substitution-hydrogen abstraction processes in the mono and tricyclic systems (45). It is possible, however, that solvation effects may remove this small, gas phase oriented difference in transition state pi energies.

The extent of substituent dependence in hydrogen abstraction from 10-substituted-9-methylanthracenes, as compared to toluene, is not easy to ascertain. While rho values for substituted anthroic acid and benzoic acid dissociation reactions reveal greater substituent dependency for the former, this same class of compounds may also experience differential solvation effects relative to substituted benzoic acids in a polar, ionizing solvent. The picture is further muddled by "field effect" transmission of substituent influences. The reaction constant for hydrogen abstraction by trichloromethyl radicals from substituted toluenes has been reported as -1.46 (46) and -1.29 (47). This is a seemingly greater substituent dependence than that for the set of anthracene compounds studied here. A major, significant variation between the two, however, lies in temperature difference with the substituted toluenes being allowed to react at a temperature some 20 degrees lower than that for the substituted methylanthracenes. Further, hydrogen abstraction occurs 450 times faster for 9-methylanthracene compared to toluene (26).

Finally, there is some controversy as to which fragment from the homolysis of bromotrichloromethane is responsible for the actual hydrogen abstraction step. Although we have followed the long accepted view that trichloromethyl radical is involved, Tanner, et al. feel that this role is filled by the bromine atom (47). Taking a different perspective, and assuming Pryor's postulate as a given, the equality of rho's between the substitution study where trichloromethyl radical is unequivocably involved and the present abstraction study would tend to exclude bromine atom as the abstracting agent. Bromine atom has demonstrated different and usually greater selectivity in direct comparison with the trichloromethyl radical. Thus the possibility that our rho value is a result of abstraction by bromine atom looms as an unlikely coincidence.

V. EXPERIMENTAL

Quantitative analyses of the kinetic trials were performed on a Varian HA-100 nuclear magnetic resonance spectrometer. Reference compounds and reagents were analyzed for purity when necessary with a Varian Aerograph 202-B gas-liquid chromatograph. Melting points were ascertained with a standard Mel-Temp apparatus.

A. Reagents and Purifications

Bromobenzene: This cosolvent was purified via vacuum distillation with the fraction employed for kinetic purposes have a boiling point of 61°-62° at 7 torr. Absence of impurities was confirmed by gas chromatography.

Fluorene: This substance was recrystallized from boiling 95% ethanol. Starting with practical Eastman Organic Chemicals grade with a melting point of 113°-116°, that obtained after purification had a melting point of 115-116.5°. A corresponding n.m.r. of the purified fluorene revealed only those peaks due to the pure compound.

Bromotrichloromethane: Reagent grade Matheson, Coleman, and Bell was used without further purification. Gas chromatography demonstrated the presence of only one compound.

para-di-tertButylbenzene: Reagent grade manufactured by Eastman Organic was employed as the internal standard in the

various runs. This compound had a melting point of 74°-76° and was used without subsequent purification.

9-methylanthracene: This substance, used for both starting material in synthesis as well as in a kinetic trial, was obtained from Aldrich and possessed a melting point of 79°-81°.

B. Compound Preparation

9,10-dimethylanthracene: A crude (90% pure) grade of anthracene from Eastman Organics was used in reaction with a mixture of paraformaldehyde and gaseous hydrochloric acid in glacial acetic acid (48). The bis-chloromethyl product obtained after a reaction time of 24 hours was (tediously) purified via successive recrystallizations from benzene. The dimethyl compound was obtained by a subsequent lithium aluminum hydride reduction of the substitution product in a dry tetrahydrofuran solution (49). Recrystallized from benzene-ethanol, the final product possessed a melting point of 182-183.5° (Lit. 184-185).

9-methyl-10-methoxyanthracene: A solution of anthrone, excess potassium hydroxide, and methyl iodid were allowed to react in an interesting procedure (50) whereby the desired end product is obtained in one step as recommended by Barnett and Cook (51). Recrystallized from light petroleum ether, the

product possessed a melting point of 138°-142° (Lit. 141-143°).

9-methyl-10-cyanoanthracene: Using the method of Fieser and Jones (52), 9 methyl-anthracene-10-carboxaldehyde was reacted with hydroxylamine to give the oxime. This, in turn, was converted to the desired product by the action of acetic anhydride (53). The compound obtained had a melting point of 208-210° (Lit. 209-210°).

9-methyl-10-acetylanthracene: A standard sequence (54) was followed in which 9-methylanthracene, acetyl chloride, and $AlCl_3$ in a benzene solution reacted to yield the desired product. The compound formed melted between 131-135° (Lit. 133-135°).

9-methyl-10-phenylanthracene: The first step here was basically the same reaction as that employed in synthesis of the bis-dichloromethylanthracene. There were two alterations from the literature preparation (55). The reaction suspension of 9-phenylanthracene, paraformaldehyde, gaseous hydrochloric acid, and glacial acetic acid employed twice the volume of acetic acid as that indicated in the procedure. This was done in order to minimize potential (reported) dimerization. The reaction time was increased four fold to 15 hours. The 9-chloromethyl-10-phenylanthracene thus obtained was reduced, as before (49), by the action of lithium aluminum hydride in dry tetrahydrofuran to 9-methyl-10-phenylanthracene. Recrystallized from benzene-ethanol, the resulting substance had a

melting point of 104-107° (Lit. 112-113°).

9-methyl-10-haloanthracenes: Both the chlorine and bromine containing materials were synthesized via the method of Mosnaim, et al. (56). Anhydrous cupric halides were prepared by drying the appropriate halide under reduced (aspirator) pressure and heating until all water was removed. The salt was then immediately transferred to carbon tetrachloride solutions of methylanthracene. The materials were allowed to react at a temperature of 78°, that of refluxing carbon tetrachloride, for 12 hours. Immediate evolution of hydrogen halide was noted by holding litmus paper over the refluxing solution. The crude products were recrystallized from light petroleum ether. The 9-methyl-10-chloroanthracene obtained melted between 177-179.5°C and the bromo analogue 169-171°C (Lit. values 180-181° and 170-172° respectively).

C. Kinetic Trials

Solutions consisting of fluorene, para di-tertbutylbenzene, the appropriate anthracene substrate, bromotrichloromethane, and bromobenzene were prepared. Actual amounts in all cases are indicated in the Appendices. The solutions were each divided among several ampoules. After nitrogen flushing during several successive freeze-thaw cycles, the ampoules were sealed under a reduced pressure of nitrogen. With an ampoule reserved for analysis of starting

material concentrations, the remaining samples were immersed in a constant temperature (70.0° ± 0.1°) oil bath. An ultraviolet lamp was placed at a distance of 20 cm from the surface of the oil, the ampoules being just under the oil's surface. After an appropriate duration of time, ranging from 2 to 4 hours depending on a given substrate's proclivity to reaction, the ampoules were cooled in a dry ice-acetone bath to quench reaction. The contents were subsequently transferred into n.m.r. tubes and a small amount of T.M.S. for the lock was added. Extents of reaction were ascertained by examining the areas of the aliphatic protons corresponding to unreacted fluorene and substituted anthracenes relative to the signal from the di-tert-butylbenzene's aliphatic protons. These areas were converted by a computer program using standard kinetics methodology into relative rates which are summarized in the Appendix.

D. Dimerization Study

As a means of ascertaining the degree to which this side reaction occurs in the absence of bromobenzene, .5390 grams of 9,10-dimethylanthracene was allowed to react in a benzene solution at a concentration simulating that typically employed in a given kinetic trial. The refluxing solution was directly illuminated with the same lamp as used in each run. Aliquots were removed at 3 subsequent 24 hour intervals. A clean spectrum emerged with both the

starting material and dimer product evident. The percentages for each interval were ascertained via the integrated area for the steadily growing peak observed at 2.02 δ, this taken to be due to the emerging aliphatic protons from the dimerization reaction.

BIBLIOGRAPHY

1. L.P. Hammett, Physical Organic Chemistry, 1st ed. McGraw-Hill, N.Y. 1940.

   also Jaffe, Chem. Rev., 53, 191 (1953).

2. C. Walling, D. Seymour, and K.B. Wolfstirn, J. Am. Chem. Soc., 79, 1544 (1948).

3. H.C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958).

4. a. M.M. Martin and G.J. Gleicher, J. Am. Chem. Soc., 86, 233 (1964). C. Walling, D. Seymour, and K.B. Wolfstirn J. Am. Chem. Soc., 70, 2559 (1948).

   b. W.C. Danen and D.G. Saunders, J. Am. Chem. Soc., 91, 5924 (1969).

   c. P.D. Bartlett and C. Ruchardt, J. Am. Chem. Soc., 82, 1757 (1960).

   d. T. Suehiro, A. Kanoya, H. Hara, T. Nakahama, M. Omori, and T. Komori, Bull. Chem. Soc., Japan, 40, 668 (1967). C.G. Swain, W.H. Stockmayer, and J.T. Clarke, J. Am. Chem. Soc., 72, 5426 (1950).

5. a. D.D. Tanner, R.J. Arhart, E.V. Blackburn, N.C. Das, and N. Wada, J. Am. Chem. Soc., 96, 829 (1974).

   b. G.A. Russell, C. DeBoer, and K.M. Desmond, J. Am. Chem. Soc., 85, 365 (1963).

   c. C. Walling, A.L. Rieger, and D.D. Tanner, J. Am. Chem. Soc., 85, 3129 (1963), and C. Walling and A.L. Rieger, ibid., 85, 3135 (1963).

   d. G.A. Russell and R.C. Williamson Jr., J. Am. Chem. Soc., 85, 2357 (1964).

   e. C. Walling and J.A. McGuinnes, J. Am. Chem. Soc., 91, 2053 (1969).

f. R.F. Bridger and G.A. Russell, J. Am. Chem. Soc., 85, 3754 (1964).

g. W.A. Pryor, U. Tonellato, D.L. Fuller, and S. Jumonville, J. Org. Chem., 34, 2018 (1969).

h. R.W. Henderson and W.A. Pryor, J. Am. Chem. Soc., 97, 7437 (1975).

i. R.W. Henderson and R.D. Ward Jr., J. Am. Chem. Soc., 96, 7556 (1974).

j. W.A. Pryor and W.D. Davis Jr., J. Am. Chem. Soc., 96, 7557 (1974).

k. W.A. Pryor, W.D. Davis Jr., and J.P. Stanley, J. Am. Chem. Soc., 95, 4754 (1973).

6. G.A. Russell, J. Org. Chem., 23, 1407 (1958).

7. M.M. Martin and G.J. Gleicher, J. Org. Chem., 28, 3266 (1963); S.S. Friedrich, L.J. Andrews and R.M. Keefer, J. Org. Chem., 35, 944 (1970); R.L. Huang and K.H. Lee, J. Chem. Soc., (c), 935 (1966); J.A. Howard, K. Ingold, and M. Symonds, Can. J. Chem., 46, 1017 (1968), also 5) f, d.

8. G.J. Gleicher, J. Org. Chem., 33, 332 (1968).

9. W.D. Totherow and G. Gleicher, J. Am. Chem. Soc., 91, 7150 (1969).

10. G.J. Gleicher, Tetrahedron, 30, 935 (1974).

11. W.S.M. Grieve and D.H. Hey, J. Chem. Soc., 1797 (1934).

12. W.A. Waters, Trans. Faraday Soc., 37, 770 (1941).

13. R.L. Dannley and M. Sternfeld, J. Am. Chem. Soc., 76, 4543 (1954).

14. R. Ito, T. Migita, N. Morikawa, and O. Simamura, Tetrahedron, 21, 955 (1965).

15. M. Anbar, D. Meyerstein, and P. Neta, J. Phys. Chem., 70, 2660 (1966), and Nature, 209, 1348 (1966), and W.T. Dixon, R.O.C. Norman, and A.L. Buley, J. Chem. Soc., 3025 (1964).

16. M.E. Kurz and M. Pellegrini, J. Org. Chem., 35, 990 (1970).

17. M.E. Kurz, P. Kovacik, A.K. Buse, and I. Kugajevsky, J. Am. Chem. Soc., 90, 1818 (1968).

18. G.A. Russell, J. Am. Chem. Soc., 80, 4987 (1958), and M.M. Martin, and G.J. Gleicher, J. Am. Chem. Soc., 86, 233 (1964).

19. D.D. Newkirk and G.J. Gleicher, J. Am. Chem. Soc., 96, 3543 (1974).

20. M. Levy and M. Swarc, J. Am. Chem. Soc., 77, 1949 (1955).

21. E.C. Kooyman and E. Farenhorst, Trans. Farady Soc., 49, 58 (1953).

22. E.C. Kooyman, Disc. Faraday Soc., 10, (1951) 163.

23. J.D. Unruh and G.J. Gleicher, J. Am. Chem. Soc., 91, 6211 (1969).

24. D.F. Church and G.J. Gleicher, J. Org. Chem., 41, 2327 (1976).

25. A. Streitweiser, Molecular Orbital Theory, John Wiley & Sons, Inc., 1961, New York. p. 328.

26. J.D. Unruh and G.J. Gleicher, J. Am. Chem. Soc., 93, 2008 (1971).

27. J.C. Arnold, G.J. Gleicher, and J.D. Unruh, J. Am. Chem. Soc., 96, 787 (1974).

28. a. M.J.S. Dewar and P.J. Grisdale, J. Am. Chem. Soc., 84, 3546 (1962).

    b. W. Adcock and M.J.S. Dewar, ibid., 89, 379 (1967).

29. G.L. Anderson, R.C. Parish, and L.M. Stock, J. Am. Chem. Soc., 93, 6984 (1971).

30. F.W. Baker, R.C. Parish, and L.M. Stock, J. Am. Chem. Soc., 89, 5677 (1967).

31. K. Bowden and D.C. Parkin, Can. J. Chem., 47, 177 (1969).

32. K. Bowden and P.C. Parkin, ibid., 47, 185 (1969).

33. L.M. Stock and H.C. Brown, Adv. Phys. Org. Chem., 1, 35 (1963).

34. W.A. Pryor, T.H. Lin, J.P. Stanley, and R.W. Henderson, J. Am. Chem. Soc., 95, 6993 (1973).

35. H. Suzuki, H. Yoneda, T. Hanafisa, and T. Sugiyama, Bull. Inst. Chem. Res. Kyoto, Univ., 54, 176 (1976). also in Chem. Abst., 86, 55195 (1977).

36. J. Trotter, Acta Cryst., 12, 237 (1959).

37. J. Trotter, Can. J. Chem., 37, 1009 (1959).

38. a. E. Bergmann, M. Rabinovitz, M. Aroney, R. LeFerre, L. Radom, and G. Ritchie, J. Chem. Soc., (B), 1551 (1968).

    b. C. Cheng, L. Murthy, and R. Ritchie, J. Chem. Soc. Faraday Trans., 2, 68, 1679 (1972).

39. G.A. Russell and C. DeBoer, J. Am. Chem. Soc., 85, 3136 (1963).

40. E.J. Bowen and D.W. Tanner, Trans. Faraday Soc., 51, 475 (1955), also J. Aladekomo, J. Lumin., 6(2), 83 (1973).

41. R. Medinger and M. Wilkinson, Trans. Faraday Soc., 61, (508), 620 (1965), and Berlman, J. Phys. Chem., 77 (4), 562 (1973).

42. H. Iwamura, M. Iwamura, S. Sato, and K. Jushida, Bull. Chem. Soc. Jap., 44, 876 (1971).

43. S.C. Dickerman and G.B. Vermont, J. Am. Chem. Soc., 84, 4150 (1962).

44. W. Offerman and F. Vogtle, J. Org. Chem., 44 (5), 710 (1979).

45. M. J. S. Dewar and C. C. Thompson, Jr., J. Am. Chem. Soc., 87, 4414 (1965).

46. E. S. Huyser, J. Am. Chem. Soc., 82, 394 (1960).

47. D. D. Tanner, R. J. Arhart, E. V. Blackburn, N. C. Das, and N. Wada, J. Am. Chem. Soc., 96, 829 (1974).

48. G. Badger and C. Cooke, J. Chem. Soc., 802, (1939).

49. J. Johnson, R. Blizzard, and H. Carhart, J. Am. Chem. Soc., 70, 3664 (1948), also M. Trevoy and H. C. Brown, J. Am. Chem. Soc., 71, 1675 (1949).

50. L. Meyer and Schlosser, Annalen der. Chemie, 420, 126 (1920).

51. L. Barnett and C. Cook, J. Chem. Soc., 2631 (192).

52. L. Fieser and S. Jones, J. Am. Chem. Soc., 64, 1667 (1942).

53. M. Wanzonek and H. Hallum, J. Org. Chem., 24, 366 (1959).

54. C. Merritt Jr. and C. E. Bram, Org. Syn. IV, 8, (1963).

55. S. Gibson, D. Mosnaim, R. C. Nonhebel, and J. A. Russell, Tetrahedron, 25, 5047 (1969).

56. D. Mosnaim, D. C. Nonhebel, and J. A. Russell, Tetrahedron, 25, 3485 (1969).

APPENDIX

Relative rates of reaction of 9, 10-dimethylanthracene relative to fluorene.

Reaction time: 3 hrs.

Temperature: 70°C

Initial mmoles $BrCCl_3$: 3450

Initial milimoles bromobenzene: 22.29

mmoles di-t-butylbenzene: .1458

Trial	Cmpd	Initial mmoles	Amt. reacted	% rxn	krel
1	10-methyl fluorene	.5223 1.048	.3665 .1243	70.171 11.864	9.579
2	10-methyl fluorene	.5223 1.048	.3600 .1178	68.924 11.249	9.793
3	10-methyl fluorene	.3223 1.048	.4189 .2178	80.196 20.787	8.949
4	10-methyl fluorene	.5223 1.048	.4105 .1969	78.607 18.798	7.406
5	10-methyl fluorene	.5223 1.048	.3754 .1427	71.877 13.620	8.664
6	10-methyl fluorene	.5223 1.048	.4226 .2115	80.911 20.185	7.345
7	10-methyl fluorene	.5223 1.048	.4264 .2347	81.634 22.402	6.682

Average: 8.060 ± 1.102

Relative rates of reaction of 10-acetyl-9-methylanthracene relative to fluorene.

Reaction time: 2 hrs

Temperature: 70°C

Initial mmoles $BrCCl_3$: 34.50

Initial mmoles bromobenzene: 19.62

mmoles di-t-butylbenzene: .1358

Trial	Cmpd	Initial mmoles	Amt. reacted	% rxn	krel
1	10-acetyl	.5797	.1235	21.305	1.349
	fluorene	1.058	.1732	16.274	
2	10-acetyl	.5797	.0816	14.074	.872
	fluorene	1.058	.1690	15.966	
3	10-acetyl	.5797	.1159	19.992	1.040
	fluorene	1.058	.2042	19.295	
4	10-acetyl	.5797	.1170	20.180	1.305
	fluorene	1.058	.1679	15.864	
5	10-acetyl	.5797	.0919	15.858	1.385
	fluorene	1.058	.1241	11.725	
6	10-acetyl	.5797	.1203	20.751	1.068
	fluorene	1.058	.2066	19.523	

Average 1.170 ± .176

Relative rates of reaction of 10-cyano-9-methylanthracene relative to fluorene.

Reaction time: 3 hrs

Temperature: 70°C

Initial mmoles $BrCCl_3$: 37.54

Initial mmoles bromobenzene: 30.31

mmoles di-t-butylbenzene: .1337

Trial	Cmpd	Initial mmoles	Amt. reaction	% rxn	krel
1	10-cyano	.5263	.3605	68.495	.534
	fluorene	1.092	.9668	88.518	
2	10-cyano	.5263	.3847	73.102	.606
	fluorene	1.092	.9669	88.534	
3	10-cyano	.5263	.3114	59.165	.539
	fluorene	1.092	.8846	80.991	
4	10-cyano	.5263	.3559	67.627	.576
	fluorene	1.092	.9383	85.910	
5	10-cyano	.5263	.3061	58.162	.574
	fluorene	1.092	.8529	78.090	

Average: 566 ± .023

Relative rates of reaction of 10-bromo-9-methylanthracene relative to fluorene.

Reaction time: 2 hrs

Temperature: 70°C

Initial mmoles $BrCCl_3$: 31.46

Initial mmoles bromobenzene: 21.40

mmoles di-t-butylbenzene: .0621

Trial	Cmpd	Initial mmoles	Amt. reaction	% rxn	krel
1	10-bromo	.2151	.1492	69.332	1.901
	fluorene	.4717	.2184	46.305	
2	10-bromo	.2151	.1493	69.383	1.547
	fluorene	.4717	.2523	53.479	
3	10-bromo	.2151	.1860	86.450	1.552
	fluorene	.4717	.3416	72.414	
4	10-bromo	.2151	.1289	59.907	1.576
	fluorene	.4717	.2076	44.004	
5	10-bromo	.2151	.1478	68.705	1.679
	fluorene	.4717	.2356	49.939	
6	10-bromo	.2151	.1583	73.606	1.808
	fluorene	.4717	.2459	52.137	

Average: 1.674 ± .119

Relative rates of reaction of 10-methoxy-9-methylanthracene relative to fluorene

Reaction time: 1 hr

Temperature: 70°C

Initial mmoles $BrCCl_3$: 30.44

Initial mmoles bromobenzene: 21.40

mmoles di-t-butylbenzene: .1621

Trial	Cmpd	Initial mmoles	Amt. reacted	% rxn	krel
1	10-methoxy fluorene	.5131 1.072	.3282 .1141	63.969 10.645	9.070
2	10-methoxy fluorene	.5131 1.072	.3503 .1920	68.284 17.910	8.308
3	10-methoxy fluorene	.5131 1.072	.4142 .1644	80.729 15.335	9.891
4	10-methoxy fluorene	.5131 1.072	.3968 .1651	77.345 15.398	8.880
5	10-methoxy fluorene	.5131 1.072	.3954 .1606	77.064 14.976	9.076
6	10-methoxy fluorene	.5131 1.072	.4750 .2754	92.881 25.683	8.763

Average: 8.998 ± .348

Relative rates of reaction of 9-methylanthracene relative to fluorene.

Reaction time: 1.5 hrs

Temperature: 70°C

Initial mmoles $BrCCl_3$: 39.57

Initial mmoles bromobenzene: 23.18

mmoles di-t-butylbenzene: .1437

Trial	Cmpd	Initial mmoles	Amt. reaction	% rxn	krel
1	9-methyl	.5250	.2400	45.707	3.208
	fluorene	1.036	.1796	17.337	
2	9-methyl	.5250	.2441	46.503	4.363
	fluorene	1.036	.1384	13.356	
3	9-methyl	.5250	.2725	51.904	3.985
	fluorene	1.036	.1738	16.779	
4	9-methyl	.5250	.2260	43.044	4.028
	fluorene	1.036	.1351	13.043	
5	9-methyl	.5250	.2614	49.793	4.695
	fluorene	1.036	.1414	13.649	
6	9-methyl	.5250	.2693	51.293	5.112
	fluorene	1.036	.1360	13.127	

Average: 4.232 ± .492
Corrected for substitution: 2.750 ± .305

Relative rates of reaction of 10-chloro-9-methylanthracene relative to fluorene.

Reaction time: 4 hrs

Temperature: 70°C

Initial mmoles $BrCCl_3$: 36.53

Initial mmoles bromobenzene: 19.62

mmoles di-t-butylbenzene: .1742

Trial	Cmpd	Initial mmoles	Amt. reaction	% rxn	krel
1	10-chloro	.5586	.2616	46.821	1.792
	fluorene	1.037	.3080	29.706	
2	10-chloro	.5586	.2795	50.042	1.910
	fluorene	1.037	.3159	30.467	
3	10-chloro	.5586	.3382	60.541	2.587
	fluorene	1.037	.3131	30.198	
4	10-chloro	.5586	.2120	37.954	2.123
	fluorene	1.037	.2087	20.133	
5	10-chloro	.5586	.2153	38.542	1.557
	fluorene	1.037	.2784	26.854	

Average: 1.994 ± .289

Relative rates of reaction of 10-phenyl-9-methylanthracene relative to fluorene.

Reaction time: 3 hrs

Temperature: 70°C

Initial mmoles $BrCCl_3$: 37.54

Initial mmoles bromobenzene: 22.29

mmoles di-t-butylbenzene: .1353

Trial	Cmpd	Initial mmoles	Amt. reaction	% rxn	krel
1	10-phenyl	.5705	.3213	56.317	1.899
	fluorene	1.051	.3713	35.345	
2	10-phenyl	.5705	.2905	50.915	1.807
	fluorene	1.051	.3420	32.551	
3	10-phenyl	.5705	.3206	56.191	1.894
	fluorene	1.051	.3711	35.325	
4	10-phenyl	.5705	.3916	68.640	2.185
	fluorene	1.051	.4326	41.175	
5	10-phenyl	.5705	.3513	61.570	1.792
	fluorene	1.051	.4345	41.358	

Average: 1.915 ± .108

Relative rates of reaction of 10-phenyl-9-chloromethylanthracene relative to fluorene.

Reaction time: 4 hrs

Temperature: 70°C

Initial mmoles $BrCCl_3$: 35.52

Initial mmoles bromobenzene: 19.62

mmoled di-t-butylbenzene: .1400

Trial	Cmpd	Initial mmoles	Amt. reacted	% rxn	krel
1	10-chloromethyl fluorene	.5431 1.031	.3527 .2475	64.946 24.00	3.820
2	10-chloromethyl fluorene	.5431 1.031	.2594 .1663	47.772 16.124	3.694
3	10-chloromethyl fluorene	.5431 1.031	.2580 .1539	47.496 14.925	3.986
4	10-chloromethyl fluorene	.5431 1.031	.3669 .2380	67.548 23.077	4.290
5	10-chloromethyl fluorene	.5431 1.031	.3252 .3235	59.870 31.364	2.426
6	10-chloromethyl fluorene	.5431 1.031	.3081 .2573	56.731 24.953	2.918

Average: 3.522 ± .567