

AN ABSTRACT OF THE THESIS OF

HELENE SOPPE-MBANG for the degree of DOCTOR OF PHILOSOPHY

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Title: MOLECULAR ORBITAL CORRELATIONS OF THE ABSTRACTION OF CHLORINE

ATOM FROM ARYLMETHYL AND HETEROARYLMETHYL CHLORIDES BY TRIPHENYL

TIN RADICAL

Abstract approved: _____

Redacted for privacy

_____ Dr. Gerald Jay Gleicher

A series of monochloromethyl arenes and heteroarenes have been reacted with triphenyltin hydride at 70° C. Under these radical conditions the only observable reaction is reduction of the starting material to arylmethane or heteroarylmethane. A significant range of relative rates (a factor of eighty) has been found among the compounds studied. The relative reactivities of the homoarylmethylchlorides can be correlated with various calculated energy differences obtained from a standard semi-empirical SCF MO method. Excellent correlations, with coefficients of at least 0.990, were obtained using several different molecular orbital models. The accuracy of these results for a nucleophilic radical is comparable to those previously obtained for hydrogen abstraction by the electrophilic trichloromethyl radical species.

The relative reactivities of the heteroarylmethyl chlorides yielded poor correlations when plotted against the same SCF calculated energy differences. Poor results were also obtained when ground state properties such as charge densities were used to correlate the data. The optimum correlation was obtained with the anion intermediate model. This suggests that a charge separated form makes an important contribution to the description of the transition state.

The relative reactivities of all compounds were treated using empirically derived four parameter equations. Poor correlation was obtained for that approach which completely neglected charge development in the transition state. However, good correlations were obtained with those models which include anionic character in the transition state. It would appear that the use of the non-alternant heteroarylmethyl systems allows for an evaluation of the importance of charge separation in free radical reactions.

Molecular Orbital Correlation
of the Relative Rates of Chlorine Atom Abstraction
from Homo- and Heteroarylmethyl Chlorides
by Triphenyltin radical

by

HELENE SOPPE-MBANG

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Typed by Jackie Poppleton for Helene Soppe-Mbang

To my family

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MOLECULAR ORBITAL CORRELATIONS
OF THE ABSTRACTION OF CHLORINE ATOM
FROM ARYLMETHYL AND HETEROARYLMETHYL CHLORIDES
BY TRIPHENYL TIN RADICAL

INTRODUCTION

Molecular Orbital Linear Free Energy Correlations of Radical Reactions

Theoretical chemists through the years have devoted great efforts in attempts to predict reaction rates and to bring more insight to the general subject of reaction mechanism. In the theory of absolute reaction rates, the rate of a reaction, k is determined by the free energy of activation ΔG^\ddagger [1] as shown by equation 1

$$k = \kappa \left(\frac{kT}{h} \right) \exp \Delta G^\ddagger / RT \quad (1)$$

ΔG^\ddagger represents the difference in energy between the reactants and the transition state. However, neither the structure nor the energy of the transition state can be determined by direct experimental methods. In 1938 Evans and Polanyi introduced an alternative procedure for the treatment of the problem of reactivity [2]. They observed that there often is a linear relationship between the free energy of activation and the free energy of the reaction

$$\Delta G^\ddagger = a + b \Delta G \quad (2)$$

If one utilizes the relation between free energy and the rate constant the result is equation 3

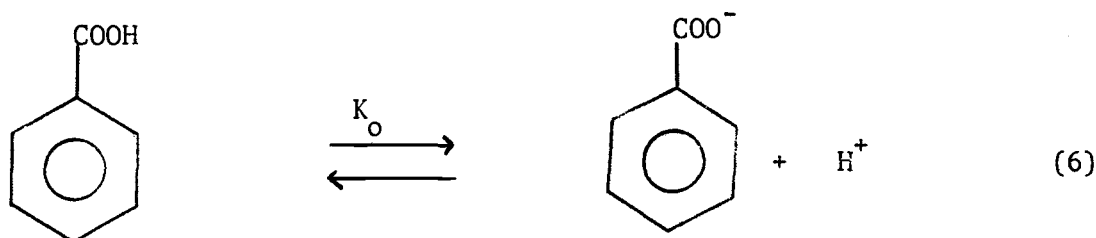
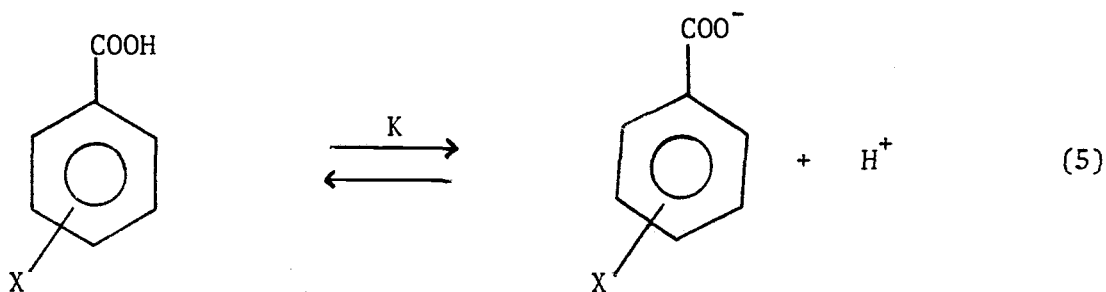
$$- RT \log k = a' + b' \Delta G \quad (3)$$

This might be considered the basis of all linear free energy relationships. It is often unnecessary to know the absolute value of ΔG or the rate since most practical chemical problems are concerned not so much with absolute rate values but with the way these quantities vary along a series of closely related reactions. It follows that b' in equation 3 is a proportionality constant which relates the rate of one compound to that of a related compound undergoing the same reaction.

The most used of the linear free energy relationships is the two parameter Hammett equation

$$\log \frac{K}{K_0} \quad \text{or} \quad \log \frac{k}{k_0} = \rho\sigma \quad (4)$$

deduced from the study of the dissociation of benzoic acids in water at 25°C [3]:

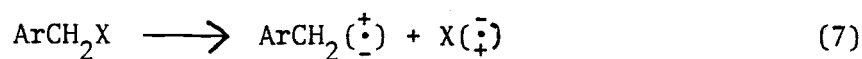


Sigma (σ) is the substituent parameter corresponding to $\log \frac{K}{K_0}$; K and K_0 are respectively the acid dissociation constant for the meta or para substituted benzoic acid and the parent acid itself. Rho (ρ) measures the sensitivity of the reaction to changes in structures. The sign of rho reflects the charge character developed at the reaction site during that particular reaction. The Hammett parameters give excellent results in correlation of reactions resembling benzoic acid dissociation, but fail to do so for other systems. Several other sets of substituents parameters have been developed. Among them are the Brown-Okamoto sigma plus parameters utilized to show direct resonance interaction between substituents and a positively charged reaction site [4] and the corresponding sigma minus parameters for reactions in which direct resonance interaction can occur between substituents and a center of negative charge [5]. Taft has also developed parameters for reactions taking place in aliphatic systems [6 a,b].

Since the early fifties, organic chemists have been extending linear free energy relationships for reactions, whose mechanism have been investigated, beyond benzene derivatives to more complex, but essentially comparable, polycyclic aromatic substrates. These, themselves, may be varied as opposed to the introduction of substituents within the same polycyclic aromatic molecule (usually benzene). This has led to correlations involving theoretically calculated quantities. These are generally determined by molecular orbital calculations and their comparisons with the relative reactivities for a chosen reaction lead to a linear free energy relationship. The original studies in this area were planned

with the so-called "one electron Hückel approximation" in mind [7]. Those correlations met with varying degrees of success. However, since the early sixties, less approximate methods have been utilized and tremendous improvement observed [8]. Irrespective of the sophistication of the method employed, one of the principles behind the molecular orbital treatment of exothermic reactions, may be viewed in the following manner. Simple chemical reactions often involve the breaking or formation of only one bond. Thus, the reactants and the transition states are closely related in structure and their Hamiltonian operators should be very similar. So if the Hamiltonian of the reactant is H that of the transition state will be $H + P$ where P is the difference between the two operators and, hopefully, must be very small. It follows that if the solutions of the Shrodinger equation for the reactant can be found, those of the transition state can be deduced using the perturbation theory. One can thus directly estimate the energy difference between the two states which is precisely what is needed [9]. This approach however, cannot be used for most of the reactions we will be dealing with as significant differences between starting material and transition state exist.

One of the major utilizations of molecular orbital theory has been in studies of the formation of arylmethyl intermediates (eq. 7) and the correlation of their rates of formation with some calculated energy difference between the arylmethyl intermediate and the parent arene [10].



If one assumes that the entropy change is constant for a series of structurally similar aromatic systems undergoing a common reaction, the Evans-Polanyi observation can be represented by equation 8

$$-RT \log k = A + C \Delta H \quad (8)$$

The constant C is often regarded as a measure of the transition state character. The enthalpy of the reaction ΔH may be calculated by molecular orbital theory, and represents the calculated energy difference between reactant and product states. For the polycyclic aromatic compounds traditionally used, the energy difference, E_{total} , can be broken into the sigma and pi components

$$E_{\text{total}} = E_{\sigma} + E_{\pi} \quad (9)$$

The sigma energy component can be calculated using localized bond models. The pi bond energy is actually the quantity usually calculated by molecular orbital theory. A large body of reactions, with well accepted mechanisms, have been treated by this type of molecular orbital approach [10].

Early examples which made use of Hückel calculations are extant. Several studies involving the formation of arylmethyl carbonium ions have been reported. Dewar and Sampson studied the solvolysis of arylmethyl chlorides in aqueous formic acid (in which the SN_1 mechanism is operating) [11], and in 80% aqueous alcohol, a less ionizing solvent (where the SN_2 solvolysis is believed to be the dominant route) [19]. Fierens and Coworkers have studied the same systems using a ternary

solvent of water, formic acid and dioxane. Here participation by water in the transition state might be expected [13]. Berliner and Shieh extended this type of analysis to 1-arylethyl chlorides undergoing solvolysis in 80% aqueous acetone [14].

An investigation on the formation of arylmethyl carbanions has been reported. Streitweiser and Langworthy examined the rates of exchange of various deuteriomethylarenes with lithium cyclohexylamide in cyclohexylamine [15]. The intermediate in this reaction is the arylmethyl lithium compound which has considerable carbanion character.

Several general conclusions have been drawn from the correlation of the rates of formation of both these charge types of arylmethyl ions with energy differences calculated by the Hückel approximation. The most significant is that a dual correlation is generally observed. Compounds with β -naphthylmethyl or benzyl structures fall on one line, and those with an α -naphthylmethyl structure fall on the other. The latter type compounds appear to be less reactive than predicted relative to their β -naphthylmethyl counterparts. Figure 1 illustrates these findings employing the generation of arylmethyl anions as an example [15]. Inclusion of non alternant, flouranthene, derivatives in the study not surprisingly generate data which cannot be accommodated by either correlation. In the present case, treatment of α -naphthyl and β -naphthyl compounds in a single correlation gave a correlation coefficient of only 0.82. If a dual correlation is used, the correlation coefficients observed are 0.97 and 0.99 for α - and β -naphthyl points respectively.

The most frequent explanation given for the observed duality is that

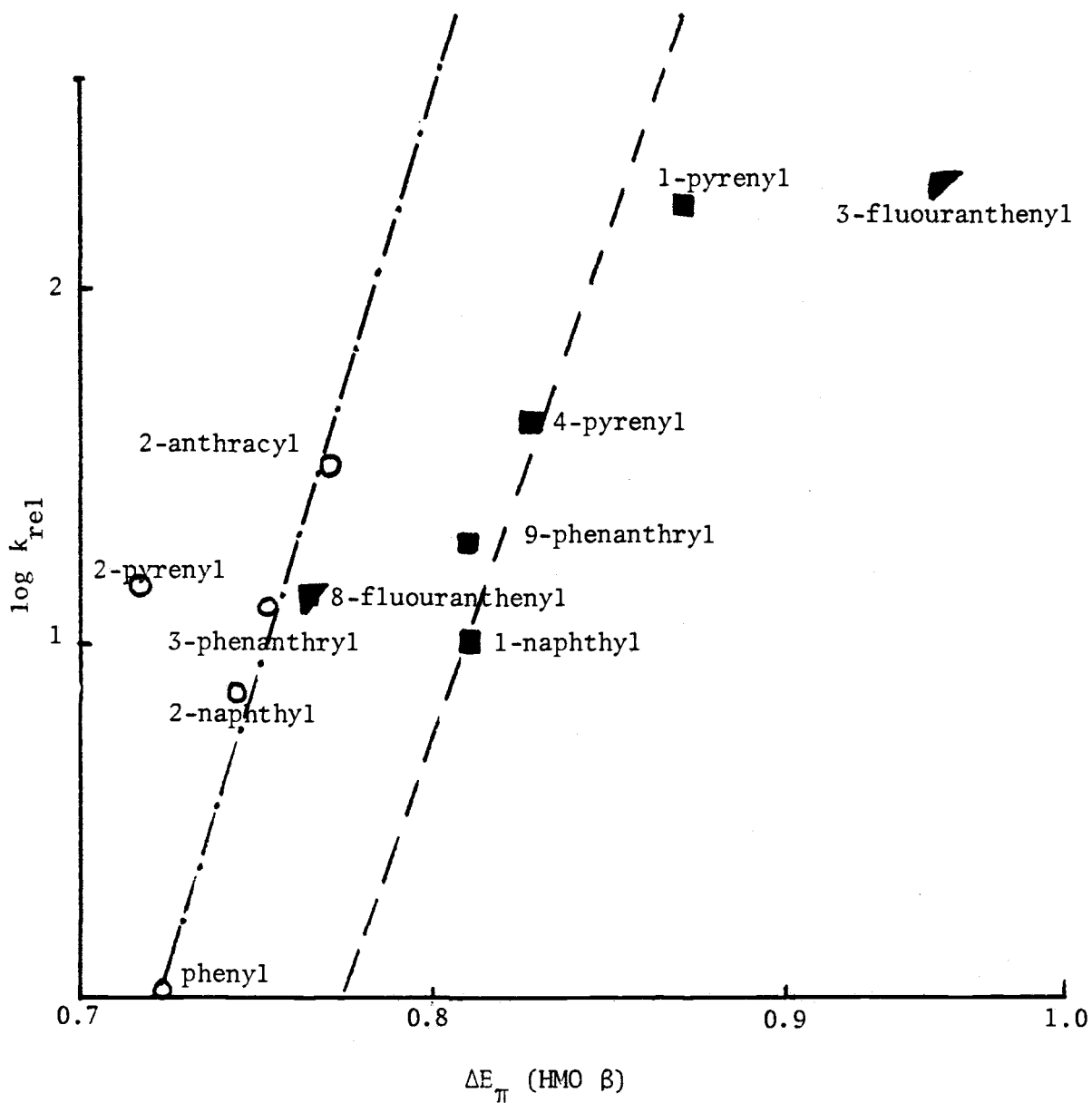
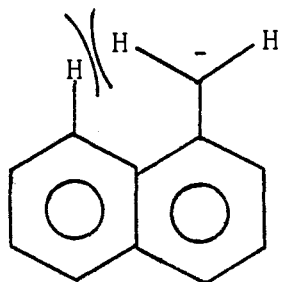


Figure 1. Correlation of the relative rates of formation of arymethyl anions with calculated HMO energy differences.

steric effects might be operating in the α -naphthyl series, which would then increase the difference in energy between ground state and transition state over that predicted solely on electronic grounds. This steric effect, called the peri effect, is a non bonded interaction between the exocyclic function and the atom or group on the other side of the point of annelation. This structural unit, common to all α -naphthyl type compounds, is illustrated below.



It is assumed that this steric effect can be lessened by an out of plane rotation of the exocyclic function. This, however, also decreases the delocalization and causes the increased energy differences observed for the α -naphthyl type systems. Streitwieser [15] in the above carbanion case estimated a rotation of seventeen degrees from planarity. A quantitative evaluation of the peri effects was undertaken some years ago. It showed that the repulsive steric interactions found in such systems are not large enough to cause the deviation observed [16].

Dewar and Thompson, using energy differences calculated by self-consistent field (SCF) molecular orbital theory, have been able to include α -naphthyl, β -naphthyl and even non-alternant species in a single correlation [17] illustrated by Figure 2. The improvement observed with

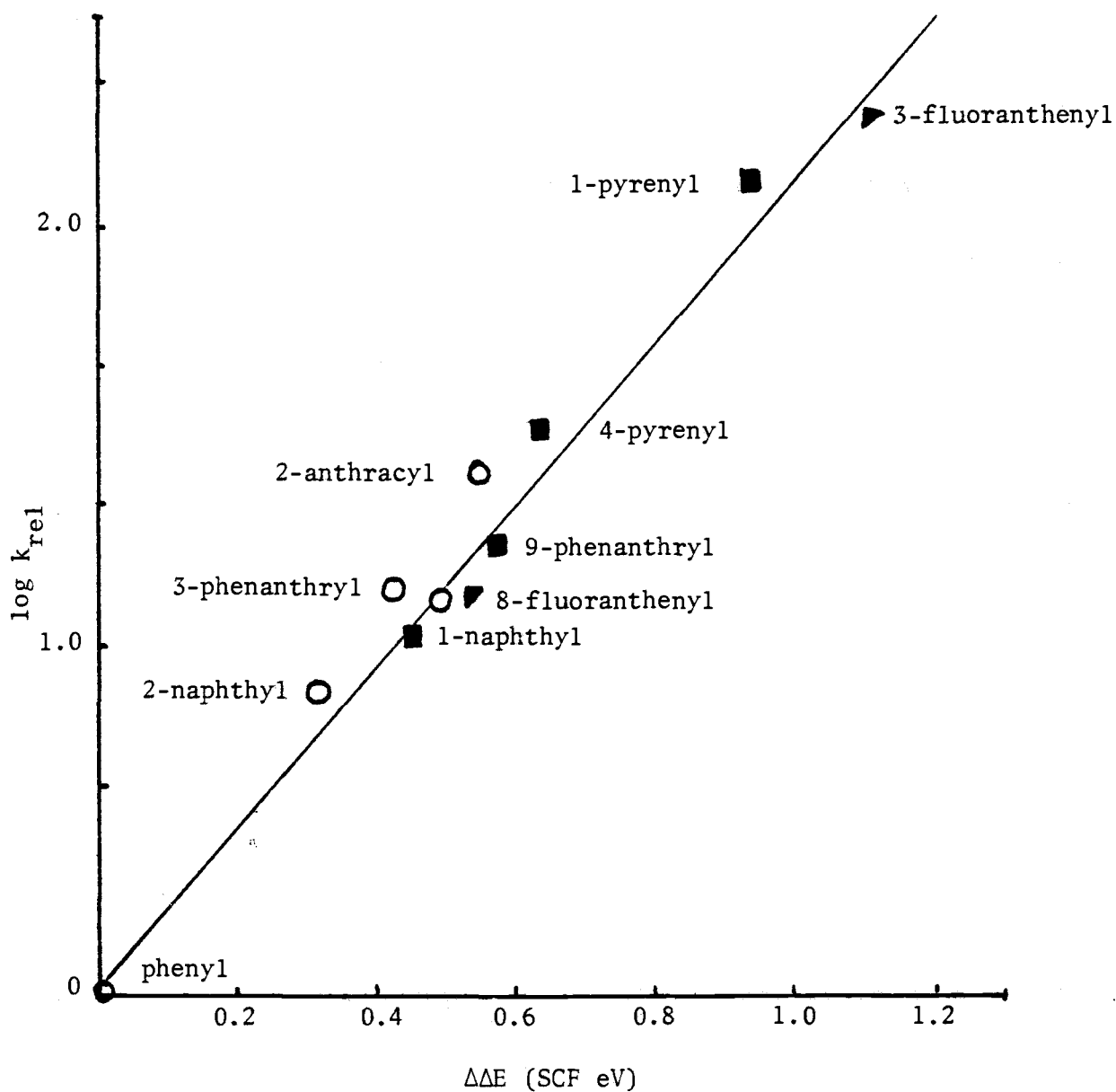


Figure 2. Correlation of the relative rates of formation of arylmethyl anions with calculated SCF energy differences.

the SCF method can best be explained by the following arguments: The matrix elements for a closed shell SCF secular determinant are given by equations 10 and 11

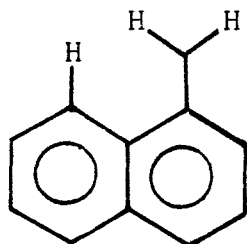
$$F_{ii} = W_{2p_i} + \frac{1}{2} q_i (ii,ii) + \sum (q_j - c_j) (ii,jj) \quad (10)$$

$$F_{ij} = \beta_{ij} - \frac{1}{2} p_{ij} (ii,jj) \quad (11)$$

W_{2p_i} is the valence state ionization potential for an electron in a carbon 2p orbital; q_i and q_j are the charge densities at atoms i and j ; c_j is the core charge at atom j , which is set equal to the number of electrons donated by that atom to the pi system (ii,jj) is the repulsion between electrons centered on atom i and on atom j ; (ii,ii) is the repulsion integral between two electrons located at atom i ; β_{ij} represents the resonance integral for an electron in an orbital between atoms i and j . It is set equal to zero unless these atoms are bonded; and p_{ij} is the bond order between atoms i and j . For alternant hydrocarbons the charge density at each position is one. It follows that the last term of the diagonal matrix elements drops out. The other two terms are constants and can be considered analogous to the Hückel alpha. In alternant hydrocarbons, the bond orders between atoms of the same set in the off diagonal matrix element drop out, and the bond order between non-bonded atoms in opposite sets are small and may have either positive or negative signs. It is therefore reasonable to assume that the off diagonal elements for bonded atoms are equal to the Hückel beta [18]. For alternant hydrocarbons there should thus be little difference between HMO and SCF

calculations. When ions on the other hand is considered, the field is no longer uniform and the charge density at each carbon atom are no longer unity. The Hückel assumption that α_i (F_{ii}) the diagonal matrix element has a fixed value characteristic of the atom breaks down. For bonded atoms with fixed internuclear separation, β_{ij} is a constant and so is (ii,jj) . This implies that the use of the Hückel β_{ij} to replace F_{ij} is justifiable. However, when the two atoms in the non-alternant are non-bonded, p_{ij} may have any value and the matrix element F_{ij} not only is no longer equal to zero but its value varies among the different atom pairs.

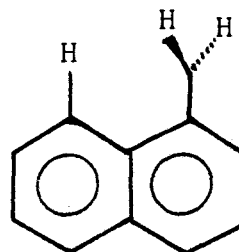
When a linear relation between bond order and bond length is assumed, the determination of the two center resonance integral and repulsion integral between pairs of bonded atoms is given added self-consistency. It is also thus possible to arrive at molecular structures as well as energies. The structures obtained from these multiple iterations tend to predict a decreased importance for the peri-interaction relative to that predicted on an assumption of constant bond length. Figure 3 illustrates this for α -naphthylmethyl. The SCF result 3C, shows that the difference observed between α -naphthyl and β -naphthyl type system previously assigned to the peri effect is not steric but rather electronic in nature. The peri effect is exaggerated in any event due to the existence of greater calculated internuclear separations for those atoms causing the repulsive interaction than is usually considered.



A) Planar, standard bond lengths

C ... H	2.44 Å
H ... H	1.71 Å
E_C ... H	0.725 Kcal/mole
E_H ... H	4.175 Kcal/mole

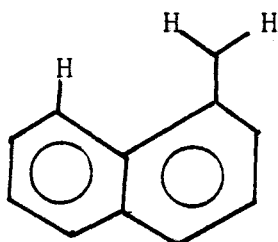
strain 4.900 Kcal/mole



B) As A, CH₂ rotated 90°

C ... H	2.44 Å
H ... H	2.74 Å
E_C ... H	0.725 Kcal/mole
E_H ... H	0.050 Kcal/mole

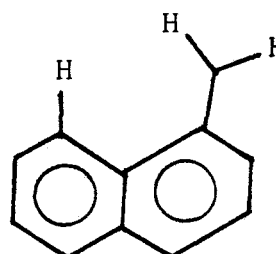
strain 0.725 Kcal/mole



C) Planar, SCF bond lengths

C ... H	2.49 Å
H ... H	1.76 Å
E_C ... H	0.529 Kcal/mole
E_H ... H	3.520 Kcal/mole

strain 4.049 Kcal/mole



D) As C, 3° in plane bends

C ... H	2.62 Å
H ... H	1.97 Å
E_C ... H	0.261 Kcal/mole
E_H ... H	1.484 Kcal/mole

E strain 1.745 Kcal/mole
angle strain 0.544 Kcal/mole

Total strain 2.289 Kcal/mole

Figure 3. Various geometries of the α -naphthylmethyl system with accompanying peri interactions and calculated strains

There also exists the possibility of removing steric strain by in plane molecular deformations which do not decrease delocalization. These are shown in figure 3D. Peri effects may be very real however, if groups larger than hydrogen are involved.

Unlike benzenoid arylmethyl ions the corresponding arylmethyl radicals are odd alternant species and the rules of alternant hydrocarbons can be applied. It is thus surprising that systematic experimental formation of arylmethyl radicals, until a few years ago, had been ignored. It might be interesting to ascertain whether the rate of formation of arylmethyl radicals could be correlated by changes in delocalization energies. It would also be important to note if the dichotomy of results between HMO and SCF approaches observed for benzylic ions also existed in the benzylic radical case. Until the report of work undertaken in our laboratory, only one attempt had been made to correlate the formation of benzylic radical systems with molecular orbital calculated quantities. Kooyman in 1953 investigated the relative rate of hydrogen abstraction from a series of aralkyl compounds and olefins by the trichloromethyl radical [19]. A correlation coefficient of only 0.47 was obtained when the author correlated the relative rate constants with calculated HMO pi energy differences between the delocalized radical (assumed to be the transition state) and the initial unsaturated compound. The poor correlation has been attributed to the utilization of a simple HMO approach and to experimental problems in evaluating the rate constants. It could also, in part, be traced to the wide range of compounds studied. Both alternant and non-alternant compounds were used. In some of these

compounds (such as triphenylmethane) complete planarity could not be achieved because of steric factors. This prevents the application of arguments based on delocalization in planar systems. It is not surprising that subsequent researchers have chosen to study compounds of greater structural similarity.

Gleicher and Unruh investigated the reactivity of a series of arylmethanes using the hydrogen abstracting reagent bromotrichloromethane as shown in equation 12 [20].



Trichloromethyl radical is believed to be the abstracting species. Tanner has proposed that bromine atom might be the abstracting agent in all reactions of bromotrichloromethane [21]. It should, however, be noted that the nature of the abstracting agent would have no effect on the correlation. The probable use of energy differences to correlate the relative rate of formation of these arylmethyl radicals is justified by the expectation that the reaction is endothermic. It was observed that the HMO approach was inadequate in correlating the formation of arylmethyl radicals even though they are alternant species. The double correlation observed for formation of arylmethyl ions is still present in the corresponding radicals. This is illustrated in Figure 4. Correlation coefficients of 0.948 and 0.904 were observed respectively for α -naphthyl and β -naphthyl points. The overall coefficient of correlation of 0.84 was however, unacceptable. The failure of the HMO approach to correlate the rate of formation of arylmethyl radicals may be attributed to the

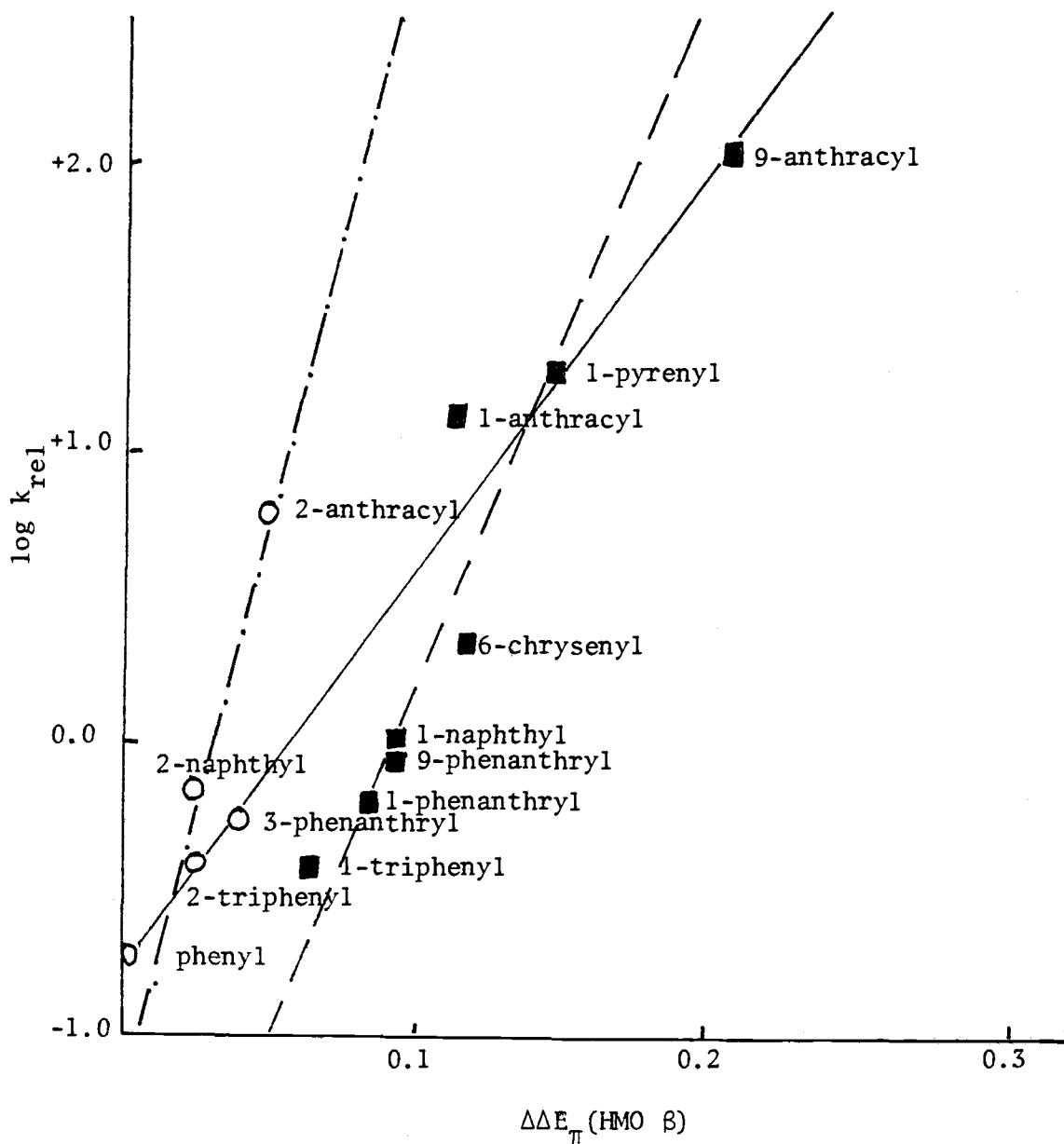
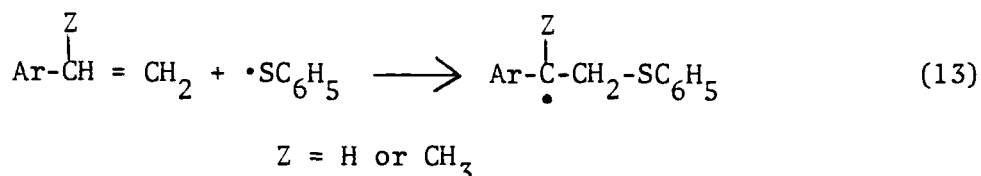


Figure 4. Relative rates of hydrogen abstraction from a series of arylmethanes by trichloromethyl radical correlated with HMO calculated energy differences.

neglect of electronic interaction terms in general. It is specifically the neglect of spin polarization in the arylmethyl radical, an odd electron system, in which there are differential interactions between electron pairs of the same and opposite spin which may cause the problem [22]. In treating the above data, a good correlation ($r = 0.977$) was observed when the energy differences were calculated by the SCF method. Figure 5 illustrates the correlation of the relative rate of hydrogen abstraction by trichloromethyl radical with SCF calculated energy differences. Gilliom's group later examined the same systems using bromine atom as the abstracting agent [23]. Similar results were obtained.

Arylmethyl type radicals have also been obtained from relatively exothermic processes. One such example is thiyl radical addition to alkenylarenes [24] shown in equation 13



As in the more endothermic case, optimum correlation was obtained with calculated energy differences rather than with any ground state or isolated molecule parameters. A correlation coefficient of only 0.4 was obtained when the free valences on the exocyclic atoms were used for correlation. Using SCF calculated energy differences, a coefficient of correlation of 0.932 (excluding 9-vinylanthracene) was observed for a single correlation. Improved values of 0.95 and 0.97 were obtained for division of the data into the traditional two sets (α -naphthyl and β -naphthyl points respectively). This indicates that in the transition state of

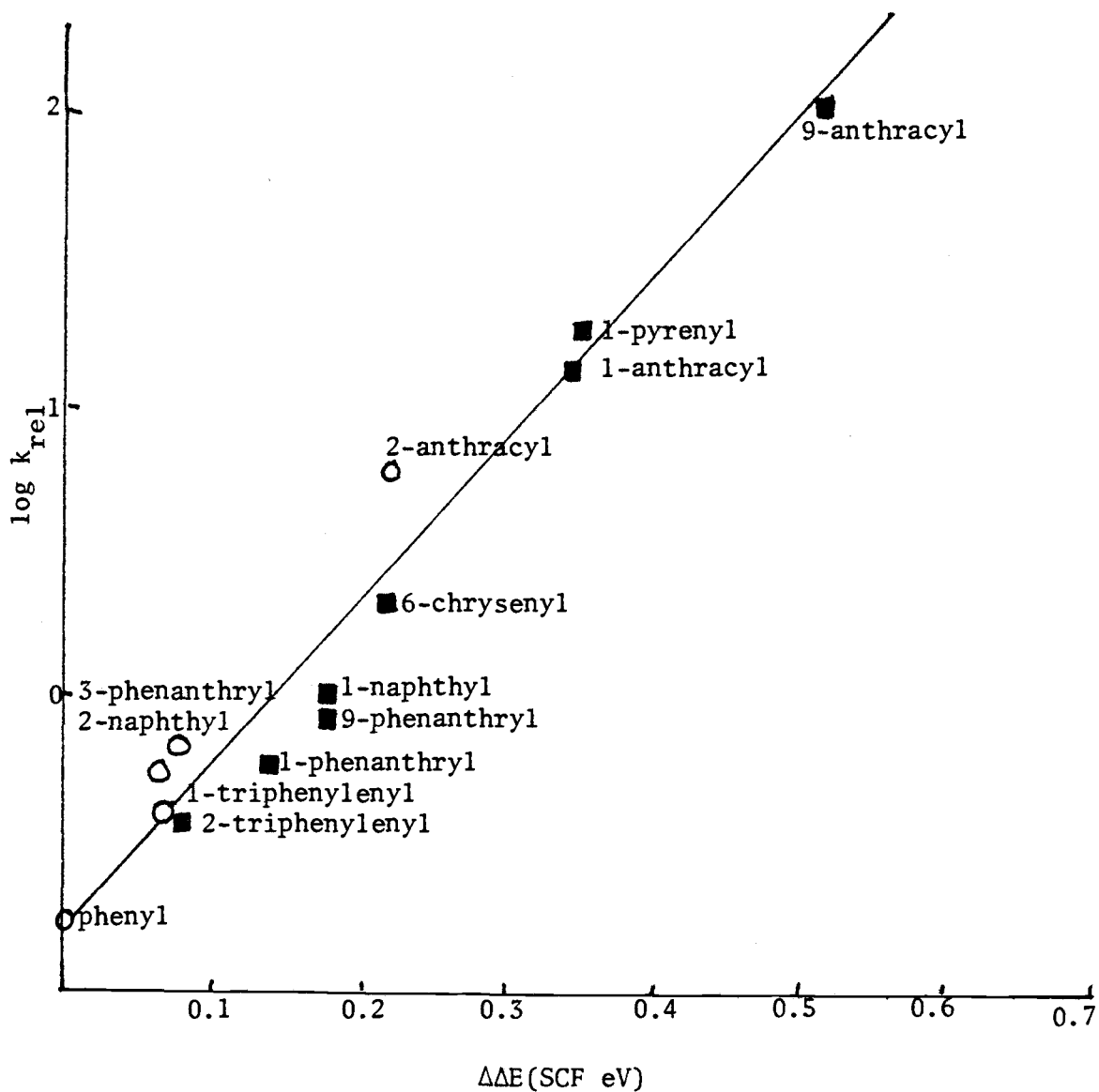


Figure 5. Relative rates of hydrogen abstraction from a series of arylmethanes by trichloromethyl radical correlated with SCF calculated energy differences.

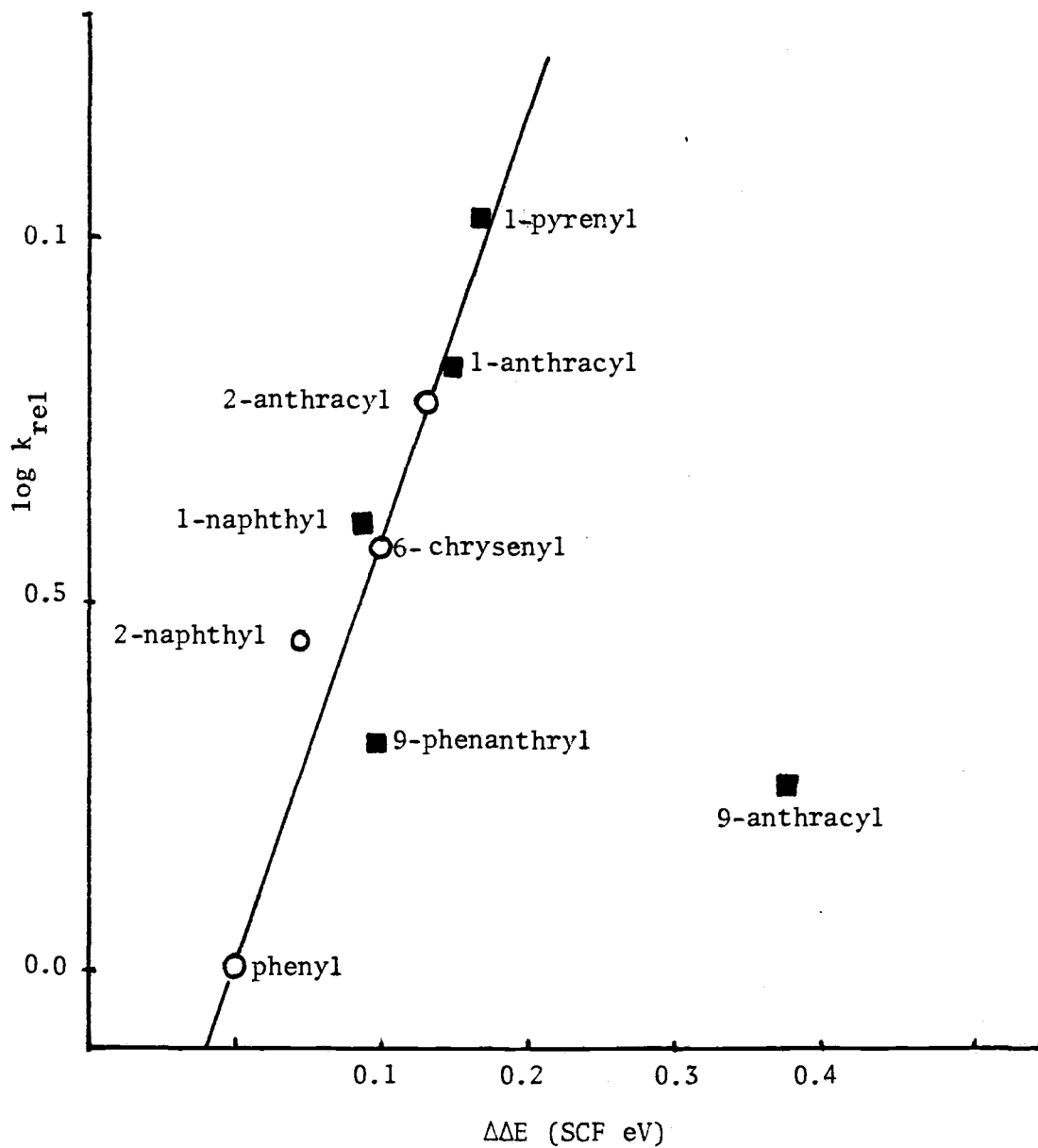
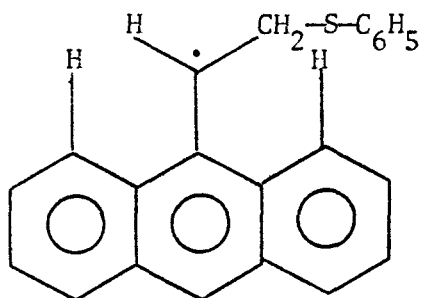
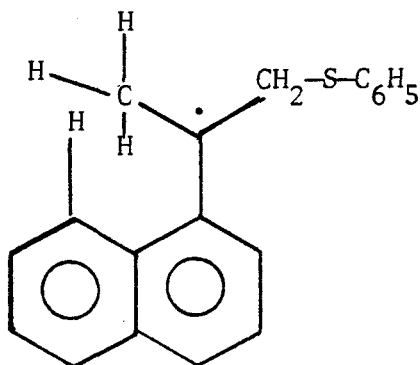


Figure 6. Relative rates of thiyl radical addition to vinylarenes correlated with SCF calculated energy differences.

this reaction there is still appreciable radical character developed. It might be inferred that peri effect will be very real in these systems, since the exocyclic portion of the transition state is no longer a simple methylene group. Indeed as can be seen from Figure 6, it is impossible to incorporate the 9-vinylanthracene within any of the above correlations because of the tremendous decrease in reactivity of this compound due to the particularly severe peri interaction.



In the α -naphthyl type compounds a small decrease in reactivity relative to the β -naphthyl type compounds might thus be expected. However, the α -naphthyl compounds may adopt conformations in which the bulky groups are directed away from the peri hydrogen. Replacement of the α olefinic proton in vinylarenes by a methyl group to produce isopropenylarenes drastically changes this situation. The structure depicted below shows that there exist no planar structure for the transition state of the thiyl radical addition to α -naphthyl type isopropenylarenes, which will not contain severe peri interactions. These compounds have been shown to react up to two powers of ten less rapidly than their β -naphthyl counterparts.



All the results cited here enforce the view that calculations which do not include interelectron terms are inadequate for correlating arylmethyl reactivity problems and that delocalization factors have the predominant role in determining the ease of formation of benzylic radicals. In those cases of arylmethyl radical generation treated to date, it also appears that ground state parameters are less successful in correlating the data.

It should be pointed out however, that there exists a branch of radical chemistry where the correlation of the relative rates of reactions with ground state parameters (e.g. charge density, bond order, free valence, self-polarizability, frontier electron density and superdelocalizability), has proven fruitful [25]. This has occurred in the correlation of substitution reactions taking place in aromatic rings. One of the best examples of this approach was reported by Kooyman [25a].

A very good correlation ($r = 0.984$) was observed when the logarithm of the relative rates of addition of trichloromethyl radical to unsubstituted, polycyclic, aromatic hydrocarbons were plotted versus the free valence indices as illustrated by Figure 7. The use of calculated energy differences rather than free valences, however, also yields a very satisfactory correlation (correlation coefficient of 0.978).

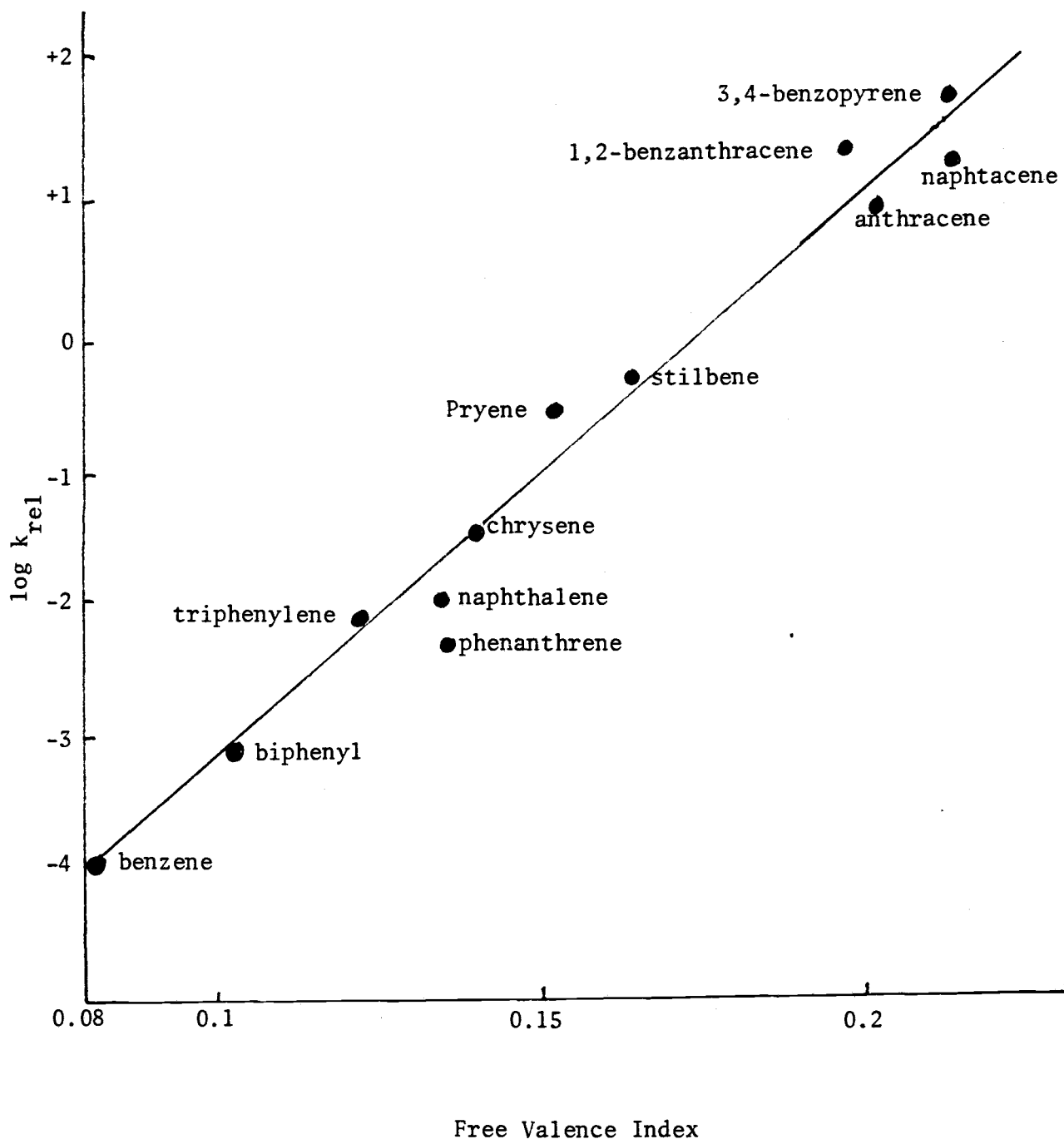
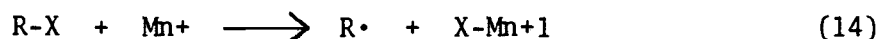


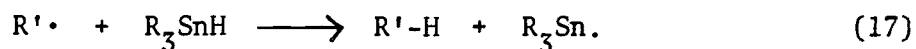
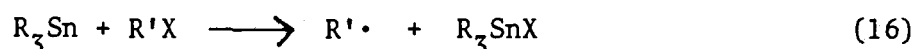
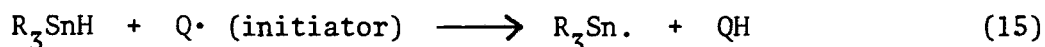
Figure 7. Relative rates of the trichloromethylation of aromatic hydrocarbons correlated with the free valence indices of the most reactive position.

Halogen Atom Abstraction by Tin Radicals

The halogen abstraction reaction by group IV A radicals is a free radical process still under active investigation. The general process may be illustrated for alkyl halides by equation 14



The reduction of alkyl halides by organotin hydrides, a synthetically useful reaction, has been shown to be closely related to hydrogen abstraction [26]. The kinetics of the reduction of a variety of halides have been studied by Carlson and Ingold who concluded that the reaction is highly selective in nature [27]. Kuivila has extensively studied the mechanism and scope of the organotin reduction of halides, and proposed a free radical mechanism since optically active α -phenylethyl chloride reacts with triphenyltin deuteride to give racemic α -deuterioethylbenzene [28]. The halogen atom is abstracted in the rate determining step in a direct manner. The mechanism is presented below.



Rabideux and co-workers reported a satisfactory Hammett correlation for the radical reduction of substituted benzyl chlorides by tributyltin hydride [29]. A rho value of +0.8 ($r = 0.98$) was observed. The transition state for the chlorine atom transfer may be described as a combination of canonical forms shown in Figure 8.

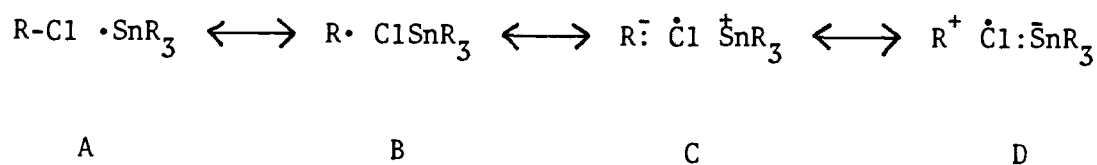
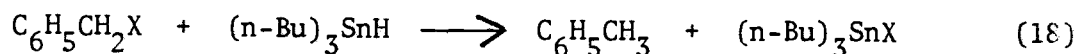


Figure 8. Structure of the transition state for the reaction of alkyl halide with a trisubstituted tin radical.

The positive rho value is consistent with the idea that the organotin radical is nucleophilic in nature and that the hybrid for chlorine abstraction by this radical includes a major contribution from the charge separated canonical structure C.

Tanner et. al., have recently reinvestigated the reduction of substituted arylmethyl halides by tributyltin hydrides [30] shown by equation 18



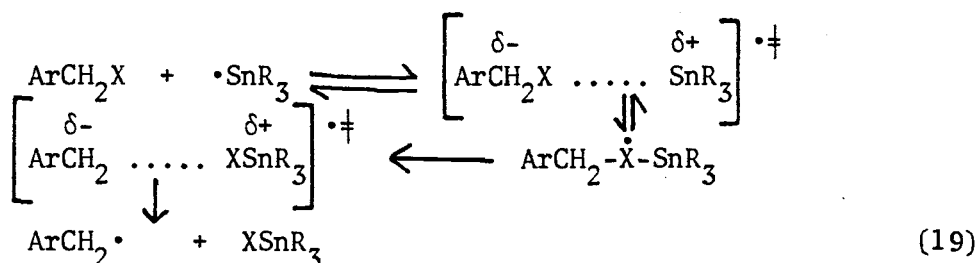
X (Cl, Br or I)

Examples of all the common halogens were studied. They observed no reduction of benzyl fluorides under their reaction conditions. Conversely the iodide atom transfer to tributyl stannyl radical shows an anomalously high rho value compared to the reactions of the corresponding chlorides and bromides as shown in Table 1.

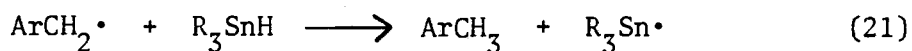
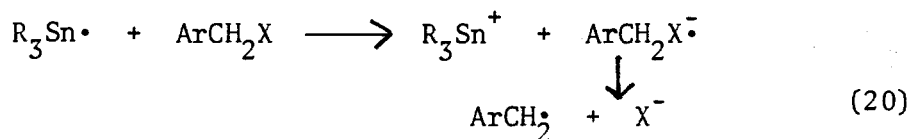
Table 1. Rho values for the reaction of α -halotoluenes with tri-n-butyltin radicals utilizing σ^- constants

α -halotoluene	$\rho(\text{rho})$	r(correlation coefficient)
α -chloro	0.34 ± 0.02	0.97
α -bromo	0.17 ± 0.02	0.98
α -iodo	0.81 ± 0.05	0.99

These rho values all correlate with sigma minus constants implying extensive charge development in the transition state. The large value of rho for iodine atom abstraction is somewhat surprising in view of the relative strengths of carbon halogen bonds. The weak bond to iodine should lead to a more exothermic reaction with decreased sensitivity to substituent changes. The iodine atom transfer was also shown to be subject to increased sensitivity toward changes in solvent polarity relative to the other halogen transfers. All these observations brought Tanner to propose two alternative mechanisms for iodine abstraction to the one proposed by Kuivila for the chlorine atom abstraction case. The first involves the formation of an intermediate with an expanded octet similar to that proposed by Sakurai for the reduction of alkyl halides with triethylgermane [31]. This is depicted in the following mechanism.



The second mechanism involves an electron transfer step shown by the following equations



Both the alternative mechanisms require that the halogen be readily able to expand its outer electron octet. Iodine may do this far more easily than the other halogens.

Kochi has used kinetic isotope effects in a complementary experiment to ascertain the extent of bond breaking and electron transfer in the reaction of methyl halides with organometallic radicals [32]. The trend of the kinetic isotope effects presented in Table 2 for chlorine, bromine and iodine transfer clearly supports Tanner's proposal.

Table 2. Carbon 13 kinetic isotope effects for halogen atom transfer from methyl halide to triphenyl tin radical.

Methyl halide	$\frac{k_{12}}{k_{13}}$
CH_3I	1.0123 ± 0.0002
CH_3Br	1.0369 ± 0.0014
CH_3Cl	1.0476 ± 0.0014

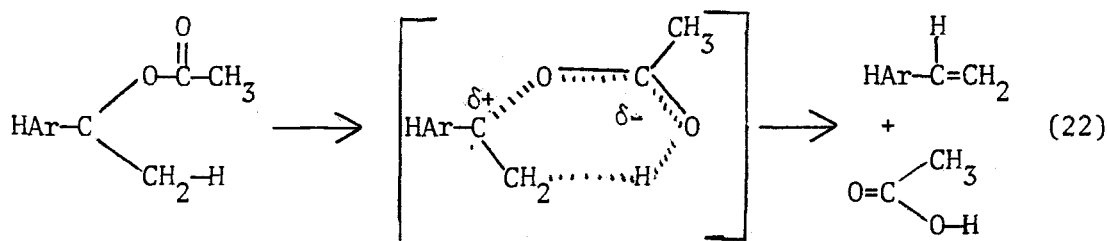
DISCUSSION OF THE PROBLEM

The studies we have made reference to in the introduction have dealt mostly, of not completely, with the formation of homoarylmethyl intermediates. The total energy of formation of these species as already indicated is made up of sigma and pi components. For alternant hydrocarbons there are well defined electronic relationships which exist among the pi electrons. In particular, there is a uniform charge density at each conjugated atom. This allows for the inference that each aryl substituent will exert a common inductive effect in a radical generating reaction [33]. Thus, any changes in reactivity can be traced solely to the differences in the ability of different groups to conjugatively stabilize the intermediate (if the usual assumption of a constant entropy is maintained). However, replacement of one or more "CH" units with isoelectronic nitrogen, oxygen or any other heteroatom destroys the uniform pi electron distribution and should change the overall inductive characteristic of the aryl groups. Thus a near inductive equivalence among heteroaryl species is not justifiable. It would be interesting to see how well molecular orbital calculations can correlate the rate of formation of heteroarylmethyl radicals. A specific question is whether the non-uniform electron distribution found in these systems can be moderately well treated by our standard technique (use of SCF calculated energy differences). A hoped for expectation would be that a single, simple molecular orbital treatment will prove able to correlate both carbocyclic and heterocyclic compounds. Alternatively, differences

caused by non-uniform electron distribution in the heterocycles might demand that new inductive and/or other correction factors be of necessity invoked.

Until very recently, the amount of pertinent experimental data dealing with the formation of heterocyclic arylmethyl intermediates in the literature was nearly non-existent. A few examples of the formation of heteroarylmethyl anions have been reported. Rigdon et al. studied the formation of 2-pyridylmethyl and 2- and 4-quinolylmethyl anions which were easily prepared from the parent methyl heterocycles by treatment with strong base [34]. These intermediates were used in condensation reactions with carbonyl compounds.

Taylor et al. have published a series of papers dealing with the systematic formation of 1-heteroarylethyl carbonium ions [35]. The reaction employed is the pyrolyses of 1-heteroarylethyl acetates. The transition state for this reaction involves appreciable generation of carbonium ion character at the benzylic position. This is shown in equation 22



Initially the pyrolyses of 1-pyridylethyl and 1-quinolyethyl acetates were studied. In both the calculations which accompanied the original paper [35a] and the subsequent theoretical paper [35b], the authors

stated that optimum correlations are found with a ground state property (charge densities) as calculated by simple HMO theory. An undefined SCF calculation was said to yield poorer results. It was implied that "energy difference" calculation were also less successful. Taylor's research group later extended the investigation to 1-isoquinolyethyl acetates, which showed a poorer correlation [35c]. Most recently a further extension to 1-(benzo[b]thienyl)ethyl acetates and 1-(benzo[b]furan-3yl)ethyl acetates has also been reported [35d]. As in the original case it is stated that the relative rates of formation of the corresponding benzylic like carbonium ions are best correlated by pi electron charge densities calculated by HMO method.

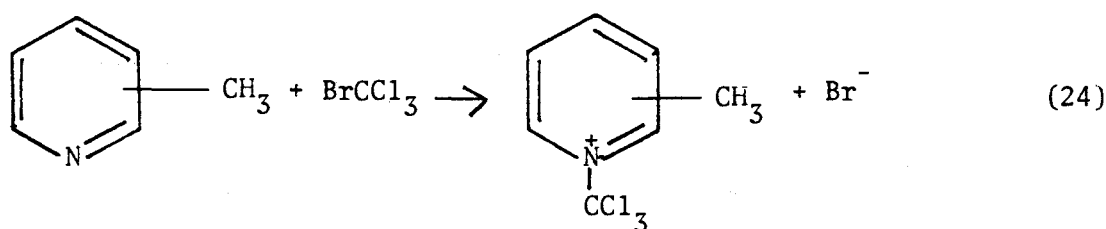
Although the correlation of the rate of formation of the 1-hetero-arylethyl carbonium with Hückel charge density is still reported to be the optimum one, Gleicher has reexamined the problem using a more advanced theoretical approach. In the light of what is known about the mechanism of the pyrolyses, the endothermicity to the reaction and the degree of probable charge development in the transition state of the reaction, the use of charge density alone to correlate the rate of the pyrolyses seems misleading. It was felt that the optimum correlation should be with a delocalization energy. SCF calculated energy differences have been carried out for the nitrogen heterocycles [36]. The new correlation obtained was appreciably superior to those of Taylor's group with regard to both correlation coefficient (0.90 versus 0.86) and standard deviation. Taylor in his latest two papers has suggested that some approach based on a combination of charge density and delocalization

energies might lead to better correlations. The rationale for this is that only incomplete charge may be developed into the transition state. This suggestion was later used by Gleicher in the empirical development of a four parameter equation as in equation 23

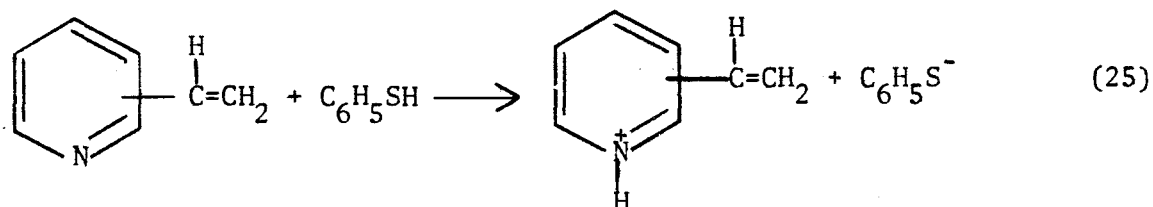
$$\log k_{\text{rel}} = 0.3917 \Delta E_t + 0.7653 q - 3.5096 \quad (23)$$

The above equation, which uses the SCF calculated energy differences and charge densities, yields calculated relative reaction rates. A comparison of these with their experimental counterparts gives a correlation with a correlation coefficient of 0.938 and an average deviation thirty percent better than its nearest competitor. It was felt that this initial result argues well for the probable ability of the theoretical approach to treat heteroarylmethyl systems without inclusion of new inductive parameters.

Unfortunately, no study dealing with the formation of heteroarylmethyl radicals have been reported to date. Gleicher and co-workers had originally hoped to extend the already presented hydrogen abstraction and thiyl radical addition studies to the nitrogen heteroaromatic systems. These attempts have proven to be unsatisfactory [37]. The three isomeric picolines showed no measurable hydrogen abstraction with bromotrchloromethane. Reaction was apparently confined to quarternization of the ring nitrogen as shown in equation 24



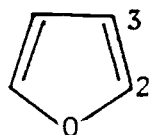
The corresponding vinylpyridines were reacted with thiophenol. Although some addition to the acyclic double bond was observed, the thiophenol was sufficiently acidic to cause proton transfer to be the predominant reaction [37].



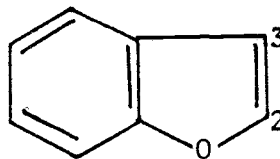
It should be noted that both the above reactions potentially involve electrophilic species which might prefer to react at the electron rich nitrogen. It logically follows that use of a "nucleophilic" radical might remove such competing processes. Chlorine atom abstraction by triphenyltin radical would be such a reaction. The triphenyltin radical should not interact with the electron rich heteroatoms.

Before directly proceeding to the actual generation of heteroarylmethyl radicals it is necessary to see whether the formation of arylmethyl radicals by halogen atom abstraction would be as amenable to molecular orbital correlations as the previously discussed electrophilic hydrogen abstraction example. It was thus planned to first investigate chlorine atom abstraction from a series of homochloromethylarenes.

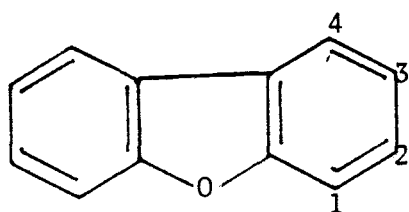
If the extension to heteroaromatic systems appears promising, it is planned to investigate as many isomeric chloromethyl derivatives of furan A, benzofuran B, dibenzofuran C, and dibenzodioxin D as is conveniently possible.



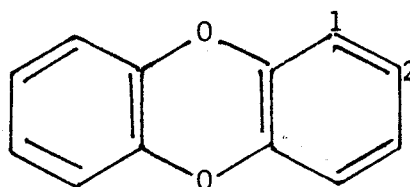
A



B

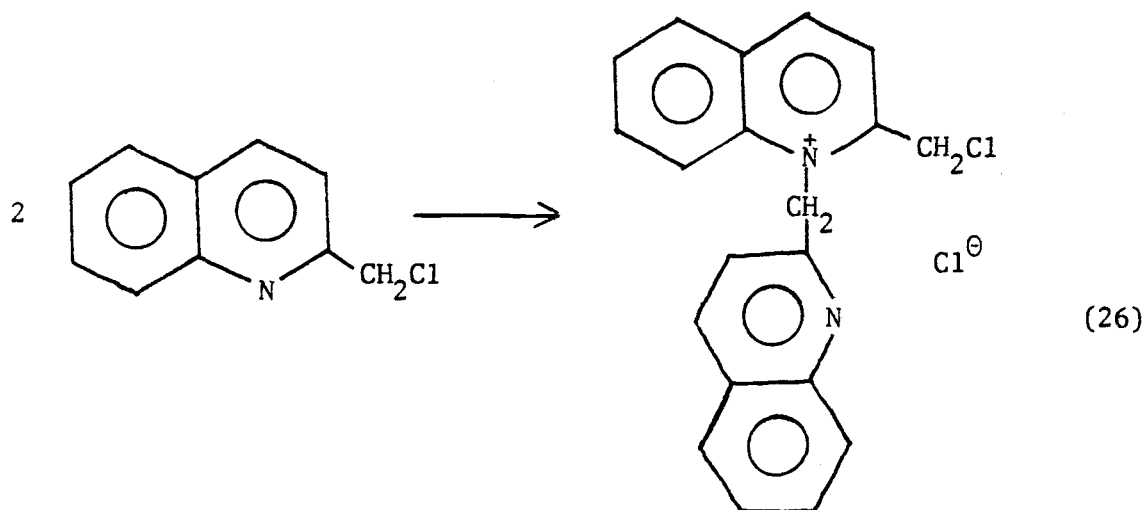


C



D

The choice of oxygen rather than nitrogen heterocycles demands explanation. Although the chloromethylpyridines, which will also be studied, are readily obtainable and reasonably stable, several of the benzologs are prepared only with difficulty [38]. As one goes from nitrogen to oxygen heterocycles, the nucleophilic character of the substrate decreases. Thus, the potential polymerization reaction shown in equation 26 (which is known to readily occur in reactive quinolines but less so in pyridines) will be non-existent in the oxygen counterparts.



The nitrogen heterocycles reactivities are also very sensitive to the acidity of the media. Bass and Nababsing have studied the homolytic methylation of quinoline in acidic and non-acidic media with *t*-butyl peroxide and lead tetraacetate as the radical sources [39]. The positional reactivities observed in non-acidic media were $8 > 4 > 5 > 2$. In an acetic acid media the reactivities of position 2 and 4 toward methylation were enhanced. In a mixture of acetic acid and hydrochloric acid, 2- and 4-methyl quinoline in equal amounts constituted at least ninety-nine percent of the product. Thus, as the acidity of the media increases the increased reactivity due to N-protonation is greater at position 2 than at position 4.

Although it is planned to carry out the chlorine atom abstraction under neutral conditions, the extreme sensitivity toward perhaps even trace amounts of acid could make interpretation of rate data difficult.

The oxygen heterocycles investigated in this work are not trivial in their own right. Particular concern may be directed toward the

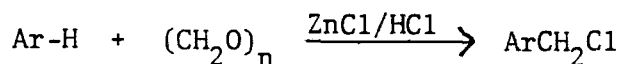
potentially important dibenzofurans and dioxins which are known for the extreme toxicity of several of their polychlorinated derivatives.

RESULTS AND DISCUSSIONS

Preparation of the Compounds

The arylmethylchlorides used in the kinetic experiments came from three sources. A few compounds such as benzyl chloride and 1-chloromethyl-naphthalene were commercially available. These were purified by distillation just prior to use. The second group of methylchlorides was prepared from the parent arene by a direct chloromethylation reaction as shown in Scheme I.

Scheme I



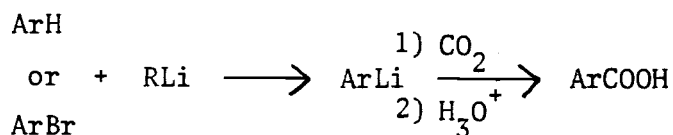
Ar = 4-phenoxyphenyl, 3-dibenzofuranyl and 2-dibenzo-p-dioxinyl.

The largest group of chloromethylarenes was synthesized from the corresponding alcohols. Some alcohols, such as the three isomeric pyridylmethanols, were commercially available. Most, however, were obtained from carboxylic acids. The latter were prepared by the following procedures.

Preparation of the Precursor Carboxylic Acids

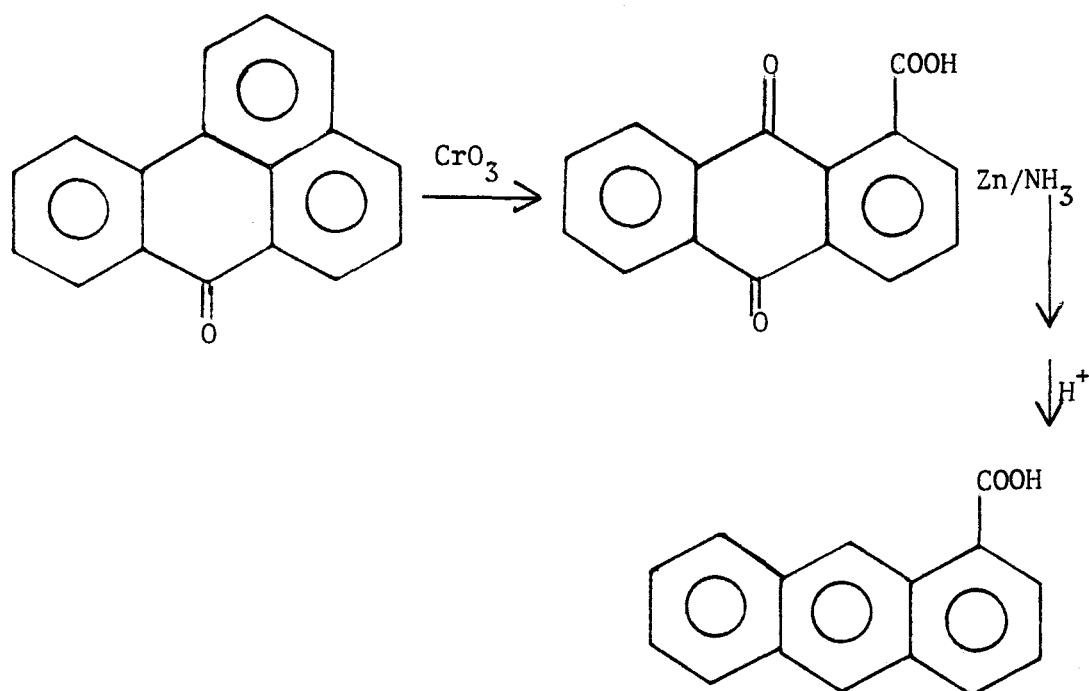
Simple carbonation of aryllithium reagents can be an effective route. In the synthesis of 2-naphthyl, 9-phenanthryl, 9-anthracyl, 1-dibenzofuranyl and 1-dibenzo-p-dioxanyl carboxylic acids, Scheme II was thus followed.

Scheme II



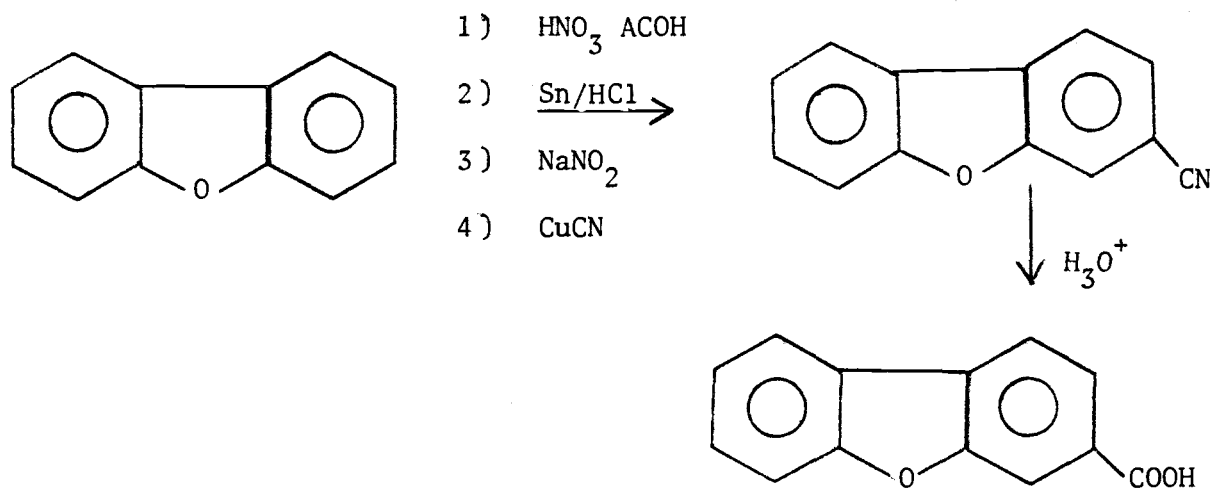
The sequence of reactions in Scheme III was used in the preparation of 1-anthracyl carboxylic acid beginning with benzanthrone [40].

Scheme III

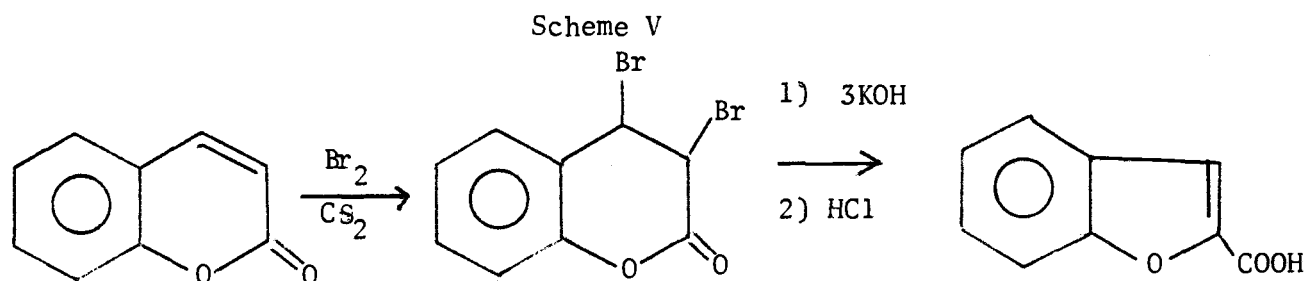


The 2-dibenzofuranyl carboxylic acid was prepared by a standard aromatic diazotisation as shown in synthetic Scheme IV [41].

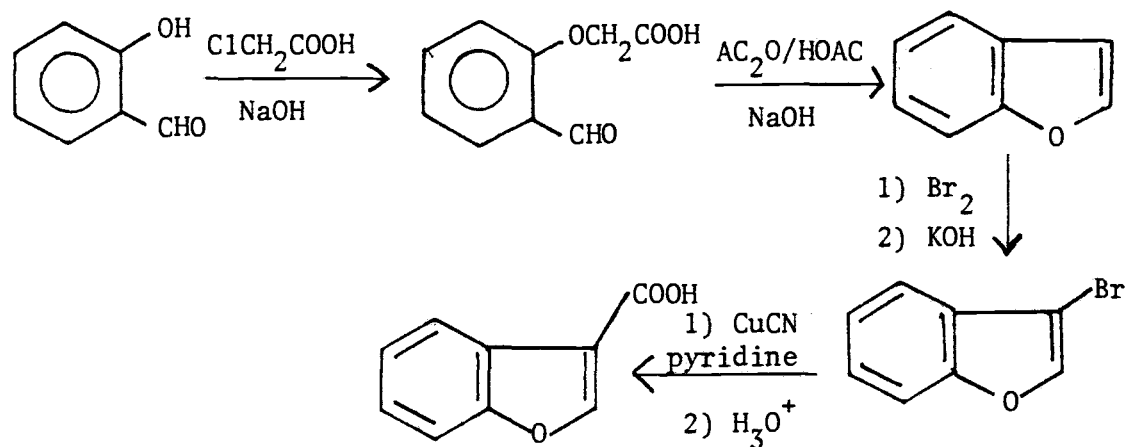
Scheme IV



The 2-benzofuranyl carboxylic acid was synthesized from coumarin in accordance with Scheme V [42]. The key step is a spontaneous rearrangement which occurs during dehydrobromination.

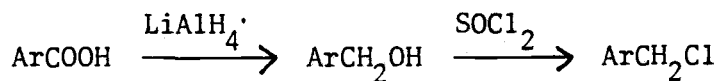


The 3-benzofuranyl carboxylic was prepared from salicylaldehyde by generation of the heterocyclic ring using synthetic Scheme VI [43].



The arylmethylchlorides could be easily prepared from the corresponding acids by Scheme VII

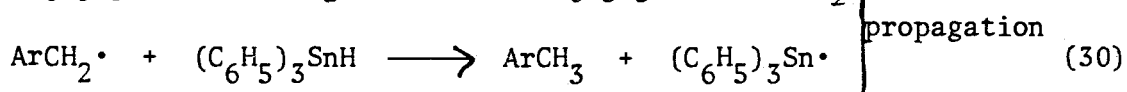
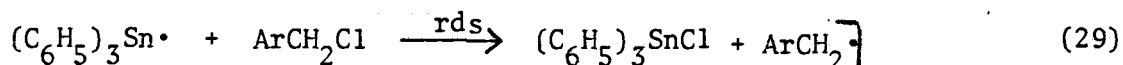
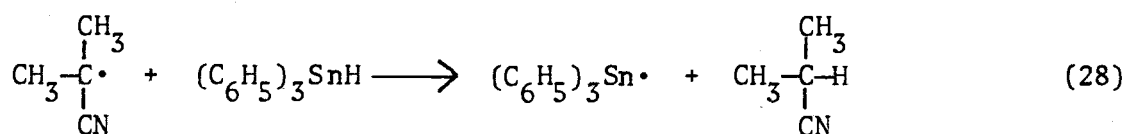
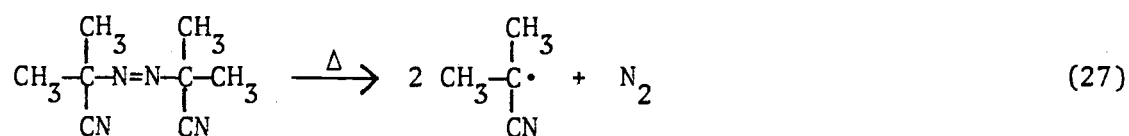
Scheme VII



All arylmethylchlorides are somewhat labile. It was found advisable to prepare them just prior to use and purify by distillation under a reduced pressure of nitrogen. Their purity could be checked by the proton nuclear magnetic resonance spectra and the infrared spectra. Details on the preparation of individual compounds are found in the experimental section of this thesis.

Relative Rates of Chlorine Atom Abstraction from a Series of Arylmethyl Chlorides by Triphenyl Tin Radical

The reaction utilized for the determination of the relative rates is the synthetically valuable reduction of organic halides by triphenyltin hydride. The reaction scheme, utilizing AIBN as an initiator, is shown in the following equations



All kinetic results were obtained by competitive techniques. Solutions of two chloromethylarenes, the internal standard, catalytic amounts of AIBN and triphenyltin hydride in benzene were prepared and placed in ampoules. The ampoules were sealed under a reduced pressure of nitrogen and reacted in a constant temperature bath at $70.0 \pm 0.2^\circ$. Reaction times varied from one to four hours which corresponds to between fifteen and seventy percent reaction of the starting materials. All the reactions were run in replicate. From these competitive studies, the relative rate of disappearance of chloromethyl arenes were obtained. The actual course

of the reaction was followed by proton nuclear magnetic resonance spectroscopy. All the analyses were carried out on a standard Varian Associates HA 100 instrument.

Before we can equate the rate of disappearance of arylmethyl chlorides to the rate of chlorine atom abstraction, it is necessary to make sure that the starting material disappears by only one route. The reactive center of the attacking radical as already mentioned is an electro-positive element. Tin radicals are known to add to alkenes [28] and the stannylation of reactive sites in polycycles must be considered as a possible, though not probable route for consumption of the reactant. A similar aromatic substitution was shown to significantly compete with hydrogen abstraction from 9-methylanthracene by the electrophilic trichloromethyl radical [44]. However, ring stannylation does not appear to be a significant problem under our reaction conditions. In competitive reaction between the anticipated least reactive halide (benzyl chloride) and anthracene (the most susceptible polycyclic) no reaction of the hydrocarbon could be determined under conditions leading to ninety-five percent disappearance of the former compound.

The ultimate product of the chlorine abstraction is some arylmethane. Compounds such as toluene and the potentially reactive 9,10-dimethylanthracene were also shown to be unreactive toward stannyl radical or the precursor hydride. It seems reasonable to consider that the only reaction taking place in the sealed ampoules is the chlorine atom abstraction.

Competitive studies between benzyl chloride and neophyl chloride were also carried out. The latter reacted only one-tenth as fast as the former compound. This strongly argues for the importance of conjugative

stabilization on the rate of formation of arylmethyl radical by halogen abstraction.

For the actual competitive studies, the signals of the benzylic protons of the chloromethylarenes under investigation (3.8δ to 5.6δ) are distinct from that of benzyl chloride the reference halide (4.5δ). The decrease in intensity of these signals relative to that of an unreactive internal standard (diphenylmethane or *t*-butylbenzene) is used to directly evaluate the ratio of rate constants by standard formulation [45]. The signals for the product arylmethanes could also be clearly observed in the range 2.3δ to 3.0δ . Material balance between halide consumed and hydrocarbons formed was approximately one hundred percent. More details can be found in the appendix. The region of the NMR spectrum below 5.6δ was inaccessible due to solvent (benzene) absorption. Table 3 contains the relative rate data obtained for a series of homocyclic arylmethyl chlorides reacting with triphenyl tin radical.

Table 3. Relative rates of chlorine atom abstraction from homoarylmethyl chlorides by triphenyl tin radical at 70°C.

System	#	Number of runs	Relative rates	$\Delta E(\text{SCF})^a$	$\Delta\Delta E(\text{SCF})$
phenyl	0	—	1	4.633	0
2-naphthyl	1	7	1.88±0.11	4.679	0.046
1-naphthyl	2	7	3.29±0.48	4.757	0.124
9-phenanthryl	3	6	3.79±0.24	4.784	0.151
1-anthracyl	4	6	7.95±0.26	4.917	0.284
9-anthracyl	5	7	38.68±2.19(b)	5.109	0.476

a) All energies given in electron volts

b) Run vs 1-anthracyl system and corrected to reference compound

The logarithms of the relative rate data may be plotted against calculated energy differences between the arylmethyl radicals and the corresponding arenes. We made use in this work of an open shell PPP SCF approach [46]. This technique allows for the determination of energy differences in both the pi and sigma portions of the system. The energies are expressed relative to the simple benzene-benzyl system. These are found in the column labeled $\Delta\Delta E$ of Table 3. Figure 9 represents the plot of the logarithm of the relative rates of formation of the homoarylmethyl radicals versus the energies expressed relative to the benzene-benzyl system. An excellent correlation is obtained with a coefficient of correlation of 0.99 and a standard deviation from the regression of only 0.11. The slope of the line is 3.136. The overall success of the correlation reaffirms the conclusion that appreciable intermediate character

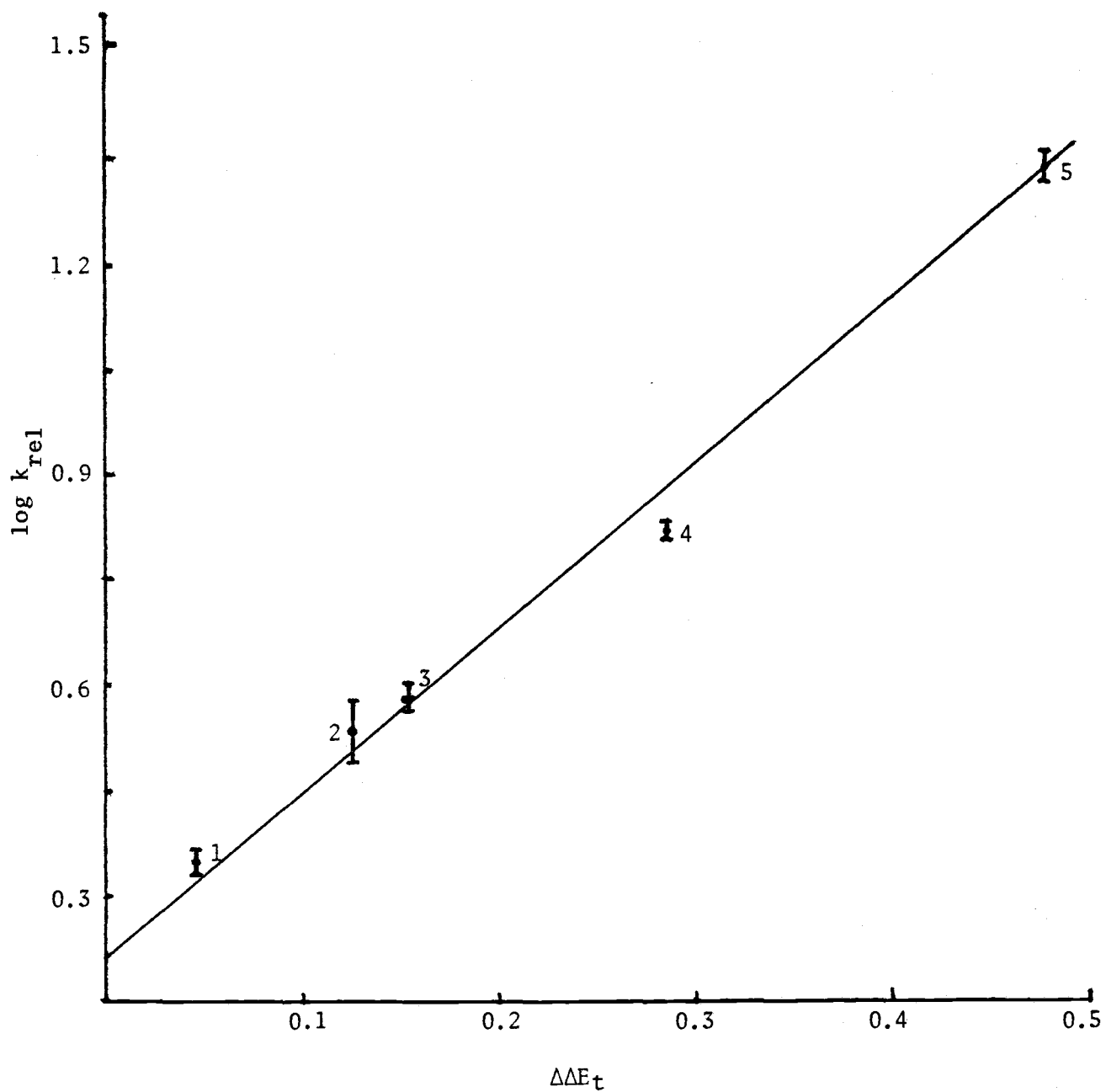


Figure 9. Logarithms of relative rates vs calculated relative energy differences for radical formation.

is developed in the transition state for halogen abstraction [47]. The possible inference that the abstraction of benzylic halogen by group IVA radicals are independent of resonance effects as suggested by Sakurai and Mochida [31] cannot be justified. The result of the correlation shows that chlorine atom abstraction by stannyl radical (nucleophilic in nature) appears to be just as amenable to molecular orbital correlations as the previously discussed electrophilic hydrogen abstraction examples. A comparison of sensitivities toward substrate modification in the hydrogen and halogen abstraction studies shows the latter process to be sixty percent of the former. This might have been adduced from earlier Hammett studies [29, 30, 21, 47], however, temperature differences in those cases make direct comparison tenuous. It is most probable that radical character is much more developed in the transition state for the hydrogen abstraction.

As already mentioned, the total energy differences discussed above include both a sigma and a pi portions. For the homocyclic compounds, similar correlations were obtained using just the pi energy or the total energy differences. The pi energy differences for the homoarylmethyl compounds can be calculated using a constant bond length model or a variable bond length model. The latter model makes use of the empirically derived bond-order bond-length relationship. This model allows for the calculation of new distances between bonded atoms (and the related electron repulsion and resonance integrals) after each iteration. An extra degree of self consistency can thus be achieved. In the constant bond length model all carbon-carbon bonds are assumed to possess a length of 1.40Å.

The variable bond length model cannot readily be used for the oxygen heterocyclic systems. This heteroatom contributes two electrons to the pi system. The bond-length bond-order relationship cannot be used here to determine resonance interactions since we cannot empirically estimate parameters for the corresponding "pure" double and single bonds. For the oxygen containing heteroarylmethyl systems, we will adopt a constant bond length model for the calculation of the pi energy differences. Carbon-carbon bonds will still be taken as 1.40\AA while the carbon-oxygen bond is assumed to have a value of 1.37\AA . To test for the adequacy of this approach we have correlated the rate of formation of the homoaryl intermediates versus energy differences calculated using both fixed bond length models and variable bond length models. The results are summarized in Table 4.

Table 4. Correlations of relative rate data for chlorine atom abstraction from homocyclic arylmethylchlorides vs calculated energy differences

System	Slope	Correlation coefficient	Standard deviation of the regression
Total energy radical	3.13 ± 0.16	0.994	0.168
Total energy anion	0.95 ± 0.05	0.994	0.054
Pi energy CBL ^a radical	3.14 ± 0.16	0.994	0.167
Pi energy CBL anion	0.95 ± 0.05	0.994	0.054
Pi energy CBL cation	3.72 ± 0.19	0.995	0.193

a) CBL is constant bond length

As can be seen in Table 4, the correlations are not very sensitive

to the choice of molecular orbital model. Equally good correlation coefficients were obtained regardless of the nature of the intermediate considered in the calculation of the energy differences. This might have been expected since the homoarylmethyl compounds studied are all alternant hydrocarbons. It should also be noted that virtually identical results are obtained (for both anion and radical cases) using total energies or the pi energies determined from the constant bond length structures. Figure 10 illustrates this for the anion model. This strongly suggests that the use of constant bond length calculations for the heterocyclic systems will introduce no appreciable error. Pyridine type molecules could be treated by either approach. For consistency, however, a constant bond length technique will again be used. The appropriate carbon nitrogen bond length is 1.38\AA .

As far as the results of the correlations of the data for the homocyclics are concerned, they show that a nucleophilic radical process is just as amenable to molecular orbital correlation as is a process utilizing electrophilic radicals. However, the correlations do not really tell us what is the nature of the transition state of the reaction. The correlations using cation, radical and anion intermediates seem to have the same reliability. The differences are in the slopes of the lines rather than the correlation coefficients. The differences in the slopes reflect an attenuation factor due to having different numbers of electrons present in the non-bonding orbital of the system and thus different degrees of repulsive interactions. The slopes of the lines, even though having no physical meaning, allows for a comparison of sensitivities toward

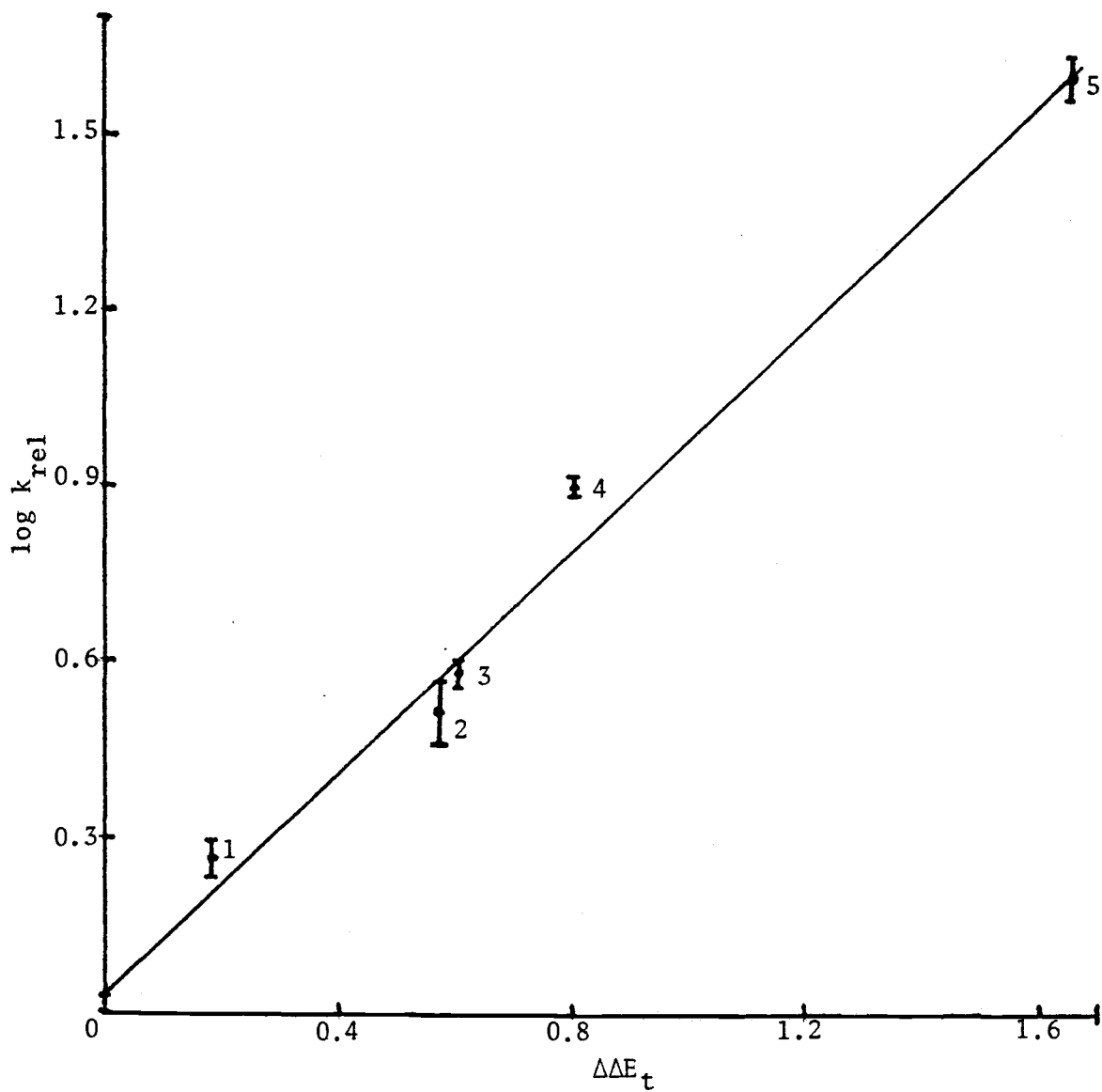


Figure 10. Logarithms of relative rates vs calculated relative energy differences for anion formation

substrate modification in the hydrogen and chlorine atoms abstraction to be made.

The invariant correlation observed in the homocyclic case for anion, radical and cation intermediates will not be expected to hold for the corresponding heterocyclic compounds, which are by definition non-alternant systems. The nature of the optimum correlation may thus give us some insight into the nature of the transition state of this nucleophilic radical process.

Relative Rates of Chlorine Atom Abstraction from a Series of Heteroaryl-methyl Chlorides by Triphenyl Tin Radical

The experimental methods and the determination of the relative rates were carried out in an identical manner to those for the homocyclic compounds. The relative rates were in most cases measured relative to 1-chloromethylnaphthalene. The values obtained were then corrected back to benzyl chloride.

Before we can study the heteroarylmethyl chlorides, it is important to show, as in the homocyclic systems, that chlorine atom abstraction is the only reaction observed.

In competitive reaction between the least reactive arylmethylchloride (benzyl chloride) and pyridine or furan, no reaction of pyridine or furan could be measured under conditions leading to ninety percent disappearance of benzyl chloride.

The ultimate product of the reaction, some heteroarylmethane (e.g. γ -picoline) was shown to be unreactive toward the triphenyl tin radical or the precursor hydride.

Competitive studies between benzyl chloride and 2-chloromethyltetrahydrofuran show that the latter reacts only one-tenth as fast as the former. This is one-thirtieth that observed for the corresponding heteroaromatic compound, 2-chloromethylfuran. This clearly shows the importance of the conjugative stabilization in the rate of formation of the heteroarylmethyl intermediate. The signals of the benzylic protons of the heteroarylmethylchlorides (3.98 δ to 4.98 δ) are distinct from that of 1-chloromethylnaphthalene the reference halide (5.00 δ). Reaction time varied from one to three hours which corresponds to between fifteen and

seventy percent reaction of the starting materials. Material balance between halide consumed and heteroarenes formed was approximately ninety percent. The relative rate data are given in Table 5.

The dibenzofuranyl and dibenzo-p-dioxinyl derivatives studied show very small differences in rate. This is probably due to the fact that the reactive center in these compounds is directly attached to a benzene ring rather than some heterocyclic unit. Their enhanced reactivity relative to benzyl chloride may be due in part to substituent effects; 4-chloromethylphenyl ether, a substituted benzyl chloride (relative rate 2.32 ± 0.04), reacts just as fast as these heteroarylmethyl chlorides. The enhanced reactivity observed for the diphenyl ether derivative relative to benzyl chloride is mostly due to the resonance effect of the para-phenoxy group. This gives some support to the view that dibenzofuran and dibenzo-p-dioxane derivatives might resemble substituted benzyl systems.

The furan and benzofuran derivatives studied, on the other hand, have the reactive center directly attached to the heterocyclic ring. In the furanyl as well as the benzofuranyl derivatives, reactivity is greater for a chloromethyl group in a position alpha rather than beta to the oxygen. This is particularly true for furan. The 2-derivative is more stabilized by resonance (and possible inductive) effects than the 3-derivative. The former effect is shown in Figure 11.

Table 5. Relative rate of chlorine atom abstraction from heteroarylmethyl chlorides by triphenyl tin radical at 70°C.

System	#	Number of runs	Relative rates	$\Delta\Delta E_{\pi}(\text{radical})^a$	$\Delta\Delta E_{\pi}(\text{anion})^a$	$\Delta\Delta q^b$
2-pyridyl	6	7	1.16±0.09	+0.236	+0.111	-0.121
3-pyridyl	7	6	1.13±0.09	+0.281	-0.025	+0.044
4-pyridyl	8	6	2.22±0.31	+0.261	+0.187	-0.057
2-furanyl	9	5	3.45±0.45	+0.525	+0.050	+0.057
3-furanyl	10	6	0.54±0.09	+0.363	-0.640	+0.031
2-benzofuranyl	11	7	4.15±0.06	+0.565	+0.480	+0.039
3-benzofuranyl	12	5	1.80±0.06	-0.426	-0.315	+0.038
1-dibenzofuranyl	13	6	2.91±0.12	+0.383	+0.176	0.028
2-dibenzofuranyl	14	5	3.41±0.09	+0.387	+0.341	-0.008
3-dibenzofuranyl	15	7	2.32±0.06	+0.359	+0.063	+0.014
1-dibenzo-p-dioxinyl	16	6	2.09±0.05	+0.359	0.095	+0.021
2-dibenzo-p-dioxinyl	17	6	2.16±0.04	+0.519	0.269	+0.003

a) Pi energies expressed relative to that of the appropriate benzene-benzyl system.

b) Relative to the charge density found at a carbon atom in any alternant hydrocarbon (1.00)

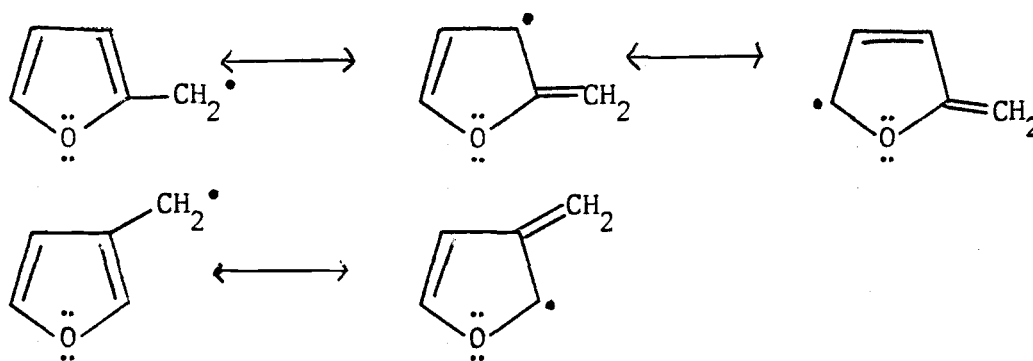


Figure 11. Resonance structures of the 2- and 3-furanylmethyl radicals.

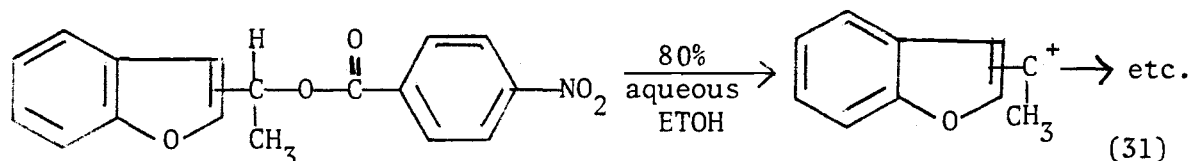
The order of reactivity observed for the chloromethylfurans is identical to that reported by Taylor [48] for the pyrolysis of 1-(2-furanyl and 3-furanyl)ethyl acetates. The similar order of reactivity observed for the furan derivatives in both processes probably reflects the extremely important role played by delocalization in the transition states.

For the benzofuranyl compounds, the 2-chloromethyl compound, which can achieve greater stabilization by inductive and resonance effects, is again more reactive than the 3-isomer. However, the difference in reactivity between the 2 and 3 isomers here is far less than that found in furan. This can be equated to the realization that the 3 position in the heterocyclic ring of benzofuran is now also a benzylic position, and thus the recipient of possible added delocalization.

Taylor (35d) has also studied the pyrolysis of 1-(2-benzofuranyl and 3-benzofuranyl)ethyl acetates. His ratio of relative reactivity is opposite to ours (0.42 versus 2.33). This could be explained on the rationale of opposite charge being developed in the transition state of the two processes. Such inductive effects seem to be less important than delocalization factors. Were this not so, a similar reversal of reactivity order

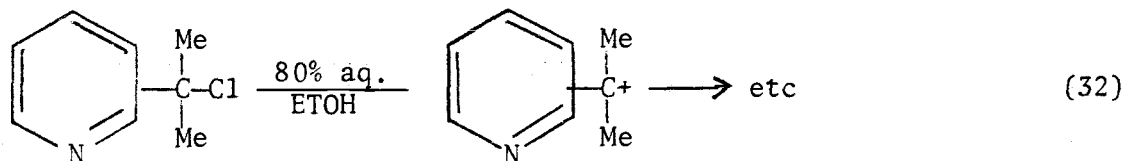
would have also been observed for the furans. Noyce [49] reported the results of a study on the solvolysis of a series of 1-arylethyl p-nitrobenzoates which included 2- and 3-benzofuranyl among the aryl groups.

This is shown in equation 31



The ratio of relative reactivities for these systems is only slightly smaller than one (0.97). The divergence with the result of Taylor probably reflects the role played by solvation of the intermediate carbonium ions in the present case.

The relative reactivities of the three pyridyl compounds show the following order: 4-pyridyl > 2-pyridyl \geq 3-pyridyl. Our results as might be expected, are opposite to those reported by Taylor (35a) for the pyrolysis of 1-pyridylethyl acetates and those of Noyce and co-workers [50] for the solvolysis of 2-pyridyl-2-chloropropane which is shown in equation 32



These reactions, in which positive charges are developed in conjugation with the heteroaryl ring, show the 3-pyridyl derivative to be the most reactive isomer. As, in the case of the previously discussed benzofuran compounds the isomeric pyridylmethyl intermediates all possess comparable

degrees of resonance stabilization. The difference observed in order of reactivity between cationic and possibly anionic processes would again reflect the inductive nature of the heteroatom.

In order to compare the results of heterocyclic systems to those of the homocyclic compounds discussed above, we attempted to correlate the relative reactivities of the heteroarylmethyl chlorides with calculated pi energy changes. A fixed bond model, as already mentioned, was used in the pi energy calculations. The correlation of the relative rates of chlorine atom abstraction versus the energy differences between the parent heteroarene and the corresponding heteroarylmethyl radical gave a slope of 1.24 and a correlation coefficient of 0.532. Utilization of the pi energy changes calculated by taking the difference between the parent heteroarene and the carbanion ion formed by the addition of one electron to the carbon centered radical was also attempted. While use of this model led to an improved correlation, the coefficient of correlation is still only 0.803. This poor correlation is, however, a large improvement over the radical model.

In view of the poor correlation observed using the energy changes, which are product state quantities, a correlation using a ground state parameter was felt to be in order. The charge density on those ring carbons attached to the chloromethyl group was the chosen parameter. This is in keeping with Taylor's suggestion that the charge density is the best ground state parameter in correlating the relative reactivities of heterocyclic systems. In the heterocyclic compounds (non-alternant) the charge density at each carbon atom is no longer equal to one as in the homocyclic compounds (alternant hydrocarbons). The almost non-existent

correlation ($r = 0.153$) obtained when the charge densities were used, argues poorly for ground state control of this reaction, although, possibly other such parameters might improve the results somewhat. The nature of the optimum correlation seems to indicate that a charge contributing form is important to the description of the transition state. This is in agreement with those results determined by the substituent effects observed by Rabideux [29] and Tanner [30] and the isotopic effects of Kochi [32]. The above results are summarized in Table 6. Figures 12 and 13 represent the correlations using the radical and anion models.

Table 6. Correlation of the relative rate data for chlorine atom abstraction from heteroarylmethyl chlorides vs calculated parameters.

Systems	Slope	Correlation Coefficient	Standard deviation of the regression
pi energy CBL radical	1.24±0.62	0.532	0.148
pi energy CBL anion	0.67±0.16	0.803	0.115
charge density CBL	0.76±1.55	0.153	0.176

Correlation of the Relative Reactivities of Homo and Heteroarylmethyl Chlorides with Calculated Parameters.

One of the goals of this work was to explore whether both homo and heteroarylmethyl intermediate formation could be related by a simple and single correlation using our standard technique (SCF calculated energy differences). It should be noted in this regard that the slopes and intercepts of the correlations obtained for the anion intermediate models for both homocyclic and heterocyclic compounds are reasonably close in value. The attempt to correlate the reactivities of both homo and heteroarylmethyl chlorides with the energy changes calculated from the radical

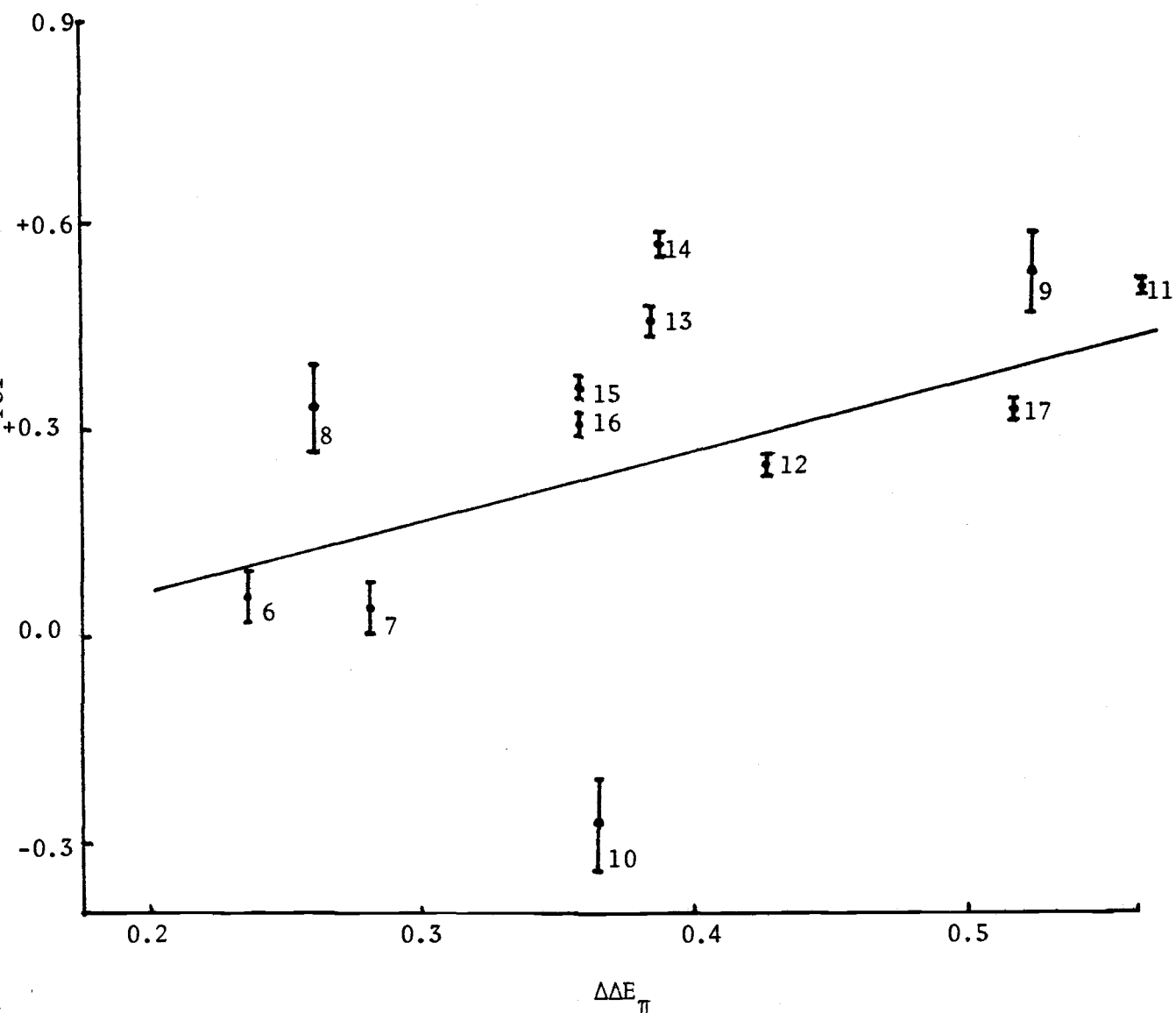


Figure 12. Logarithms of the relative rates of formation of heteroaryl-methyl radicals vs calculated relative energy differences.

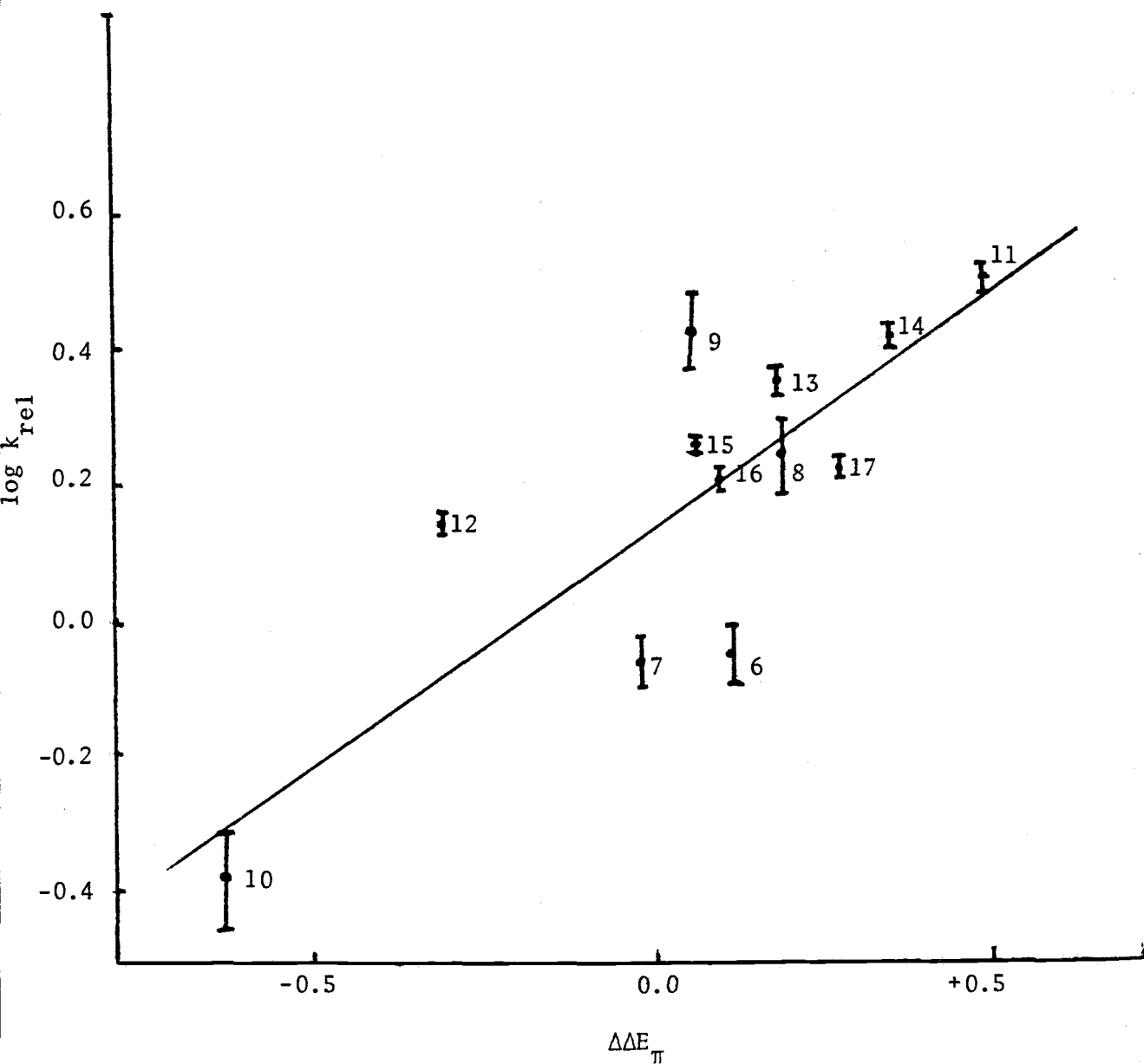


Figure 13. Logarithms of the relative rates of formation of heteroarylmethyl anions vs calculated relative energy differences.

model gave a correlation coefficient of 0.411. This is poorer than the one observed when the heterocyclic systems were treated alone. A more productive case was the attempted correlation of all relative rates using the carbanion model. A coefficient of correlation of 0.929 which is fairly good was obtained. These results shown in Table 7 give additional support to the idea that there is development of negative charge character in the transition state of the chlorine atom abstraction by triphenyl tin radical. These correlations are illustrated in Figures 14 and 15.

Table 7. Correlation of the relative rate data for chlorine atom abstraction from both homo and heteroarylmethyl chlorides vs calculated energy changes.

System	Slope	Correlation coefficient	Standard deviation of the regression
All points pi energy CBL radical	1.03 ± 0.57	0.411	0.244
All points pi energy CBL anion	0.76 ± 0.075	0.929	0.115

The fair correlation observed for the anion model can be interpreted to mean that there is not only extensive carbon-chlorine bond breaking in the transition state of this process, but appreciable negative charge character at the reactive carbon. It also seems that the formation of homo and heteroarylmethyl intermediates can be combined into a single molecular orbital correlation.

In view of the modest correlation observed, even in the anion model, relative to the results obtained for the homocyclic systems alone, it seems potentially productive to investigate whether other factors might

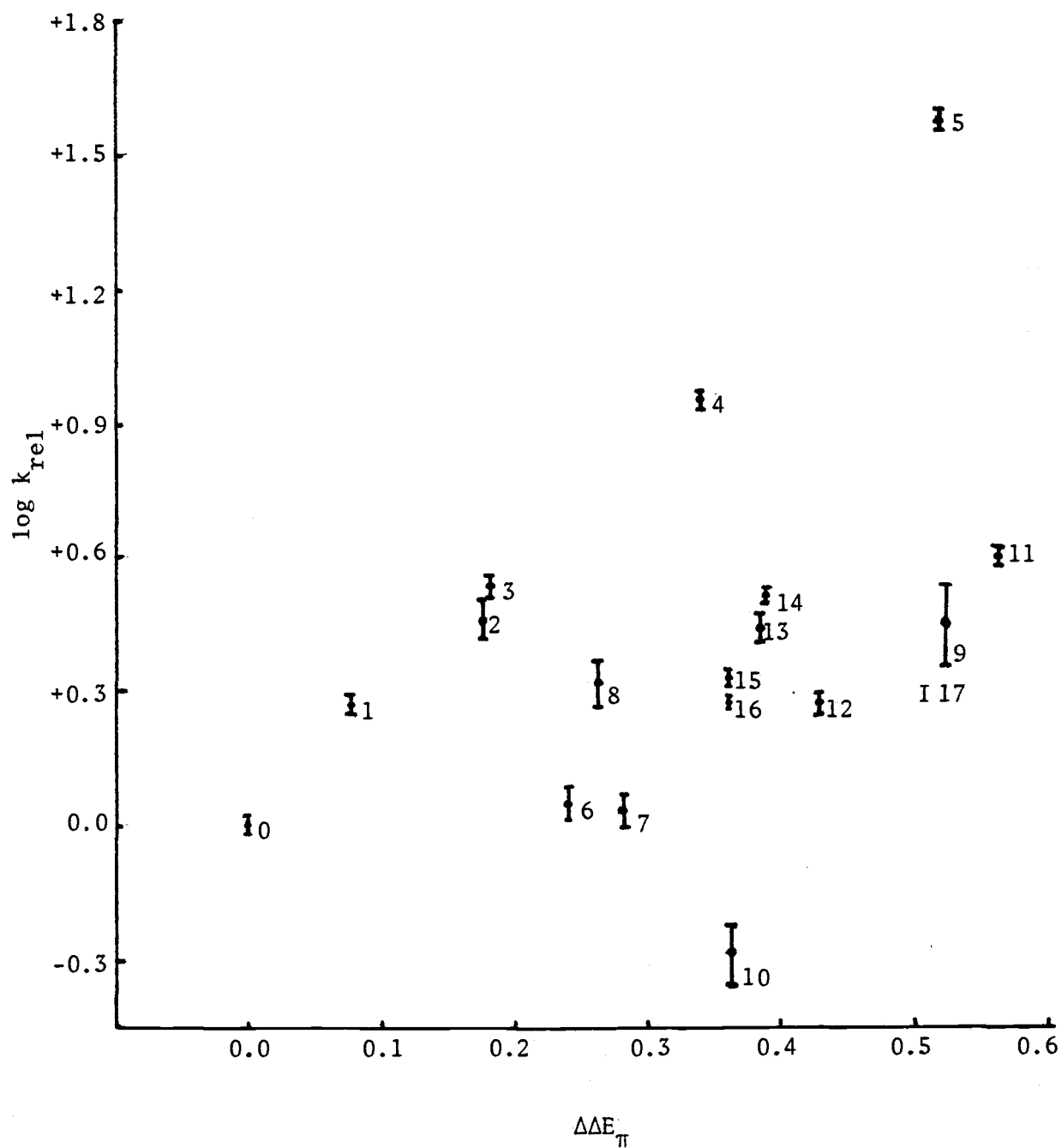


Figure 14. Logarithms of the relative rates of formation of homo and heteroarylmethyl radicals vs calculated relative energy differences.

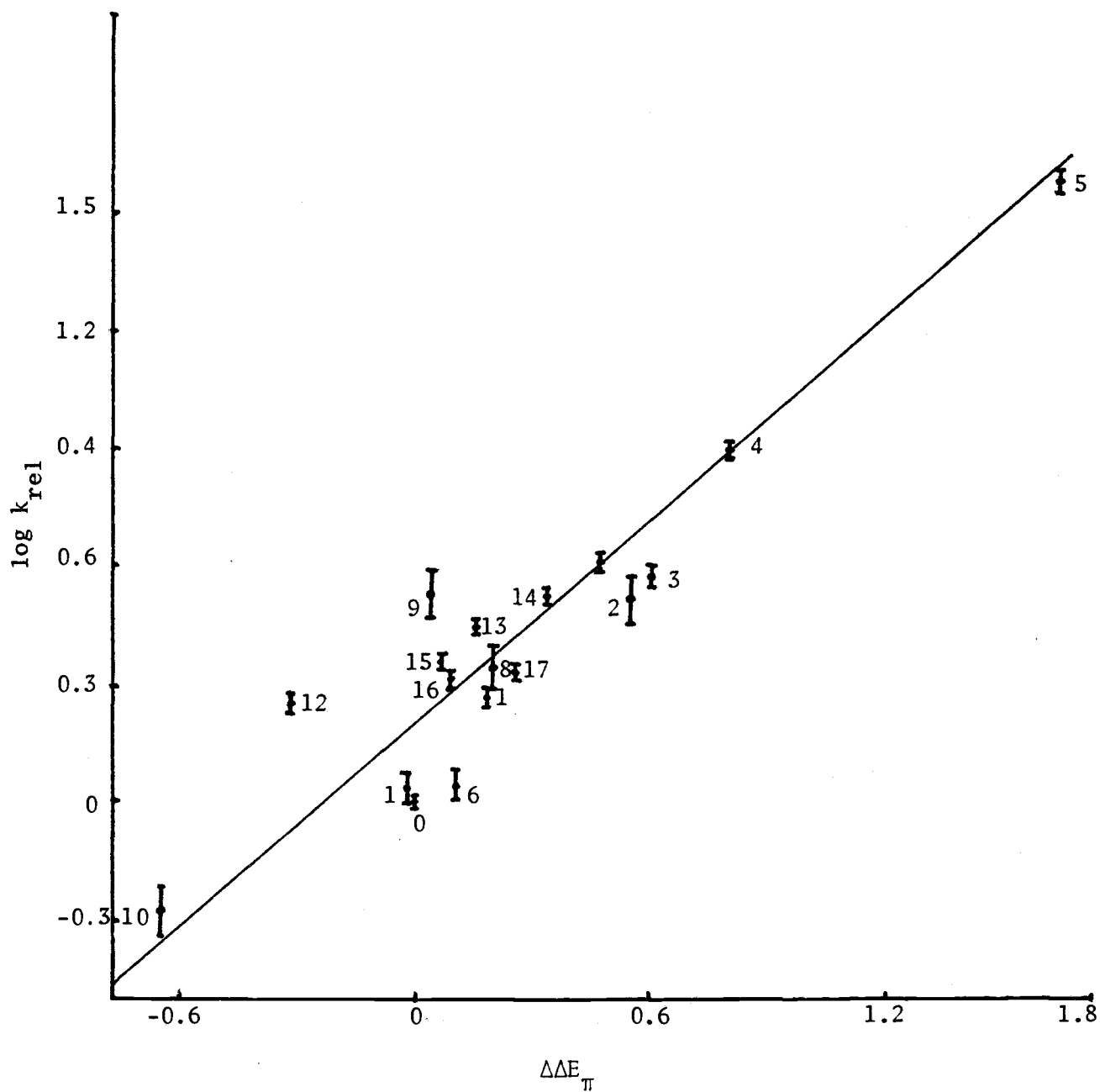


Figure 15. Logarithms of the relative rates of formation of homo and heteroarylmethyl anions vs calculated relative energy differences.

play a significant role in determining the rates of the chlorine atom abstraction. Two approaches were considered. Since the chlorine atom abstraction has been shown to have an earlier transition state than the closely related hydrogen abstraction, a correlation with a model including not only the pi energy changes but also some ground state parameter might be in order. In keeping with Taylor, we once again considered the charge density as the best ground state parameter to use. The halogen abstraction by tin radicals has been shown to have polar character. Any treatment of the transition state should thus reflect his dual radical and anionic nature. It might be instructive to therefore devise an equation similar to that proposed by Yukawa and Tsumo [51] for Hammett correlation, which could reflect the transition state sensitivity to both radical and anionic factors.

To test the above approaches, four parameter equations of the form shown in equations 33 and 34 were developed by curve fitting the available data.

$$\log k_{rel} = A(\Delta\Delta E_{\pi}) + B(\Delta q) + C \quad (33)$$

$$\log k_{rel} = A(\Delta\Delta E_{\pi})_{anion} + B(\Delta\Delta E_{\pi})_{radical} + C \quad (34)$$

The value of A, B, and C were found in an iterative fashion, where A and B were alternatively held constant so that new values of the others could be determined. This was continued until self-consistent values of the parameters were obtained. The final values are shown in equations 35, 36, and 37

$$\log k_{rel} = 1.137\Delta\Delta E_{\pi_{radical}} + 1.131\Delta q + 0.048 \quad (35)$$

$$\log k_{rel} = 1.137\Delta\Delta E_{\pi_{anion}} + 1.963\Delta q + 0.205 \quad (36)$$

$$\log k_{rel} = 0.765\Delta\Delta E_{\pi_{anion}} + 0.515\Delta\Delta E_{\pi_{radical}} + 0.025 \quad (37)$$

The calculated logarithms of the relative rates were plotted against the experimental values as illustrated by Figures 16, 17, and 18. The results of these correlations are shown in Table 8.

Table 8. Correlation coefficient of the relative rate data vs the calculated relative rates derived from the four parameter equations.

System	Slope	Correlation	Standard deviation of the regression
pi energy + Δq radical	1.000	0.425	0.53
pi energy + Δq anion	0.997	0.953	0.08
pi energy radical + anion	1.000	0.962	0.07

The most notable finding in Table 8 is the extremely poor result found in the double correlation which utilized radical intermediate energy differences and charge densities. It is significant that this is the only approach which completely ignores charge development in the transition state of the reaction. Nearly equally good, improved correlations were found using the other two four parameter equations. The slightly better correlation was found from equation 37. This would seem to suggest a transition state which is intermediate between simple radical and anion models in its structure, with the latter playing the larger role. The correlation resulting from the use of equation 36 must here be interpreted in somewhat different terms. The use of energy difference-charge density

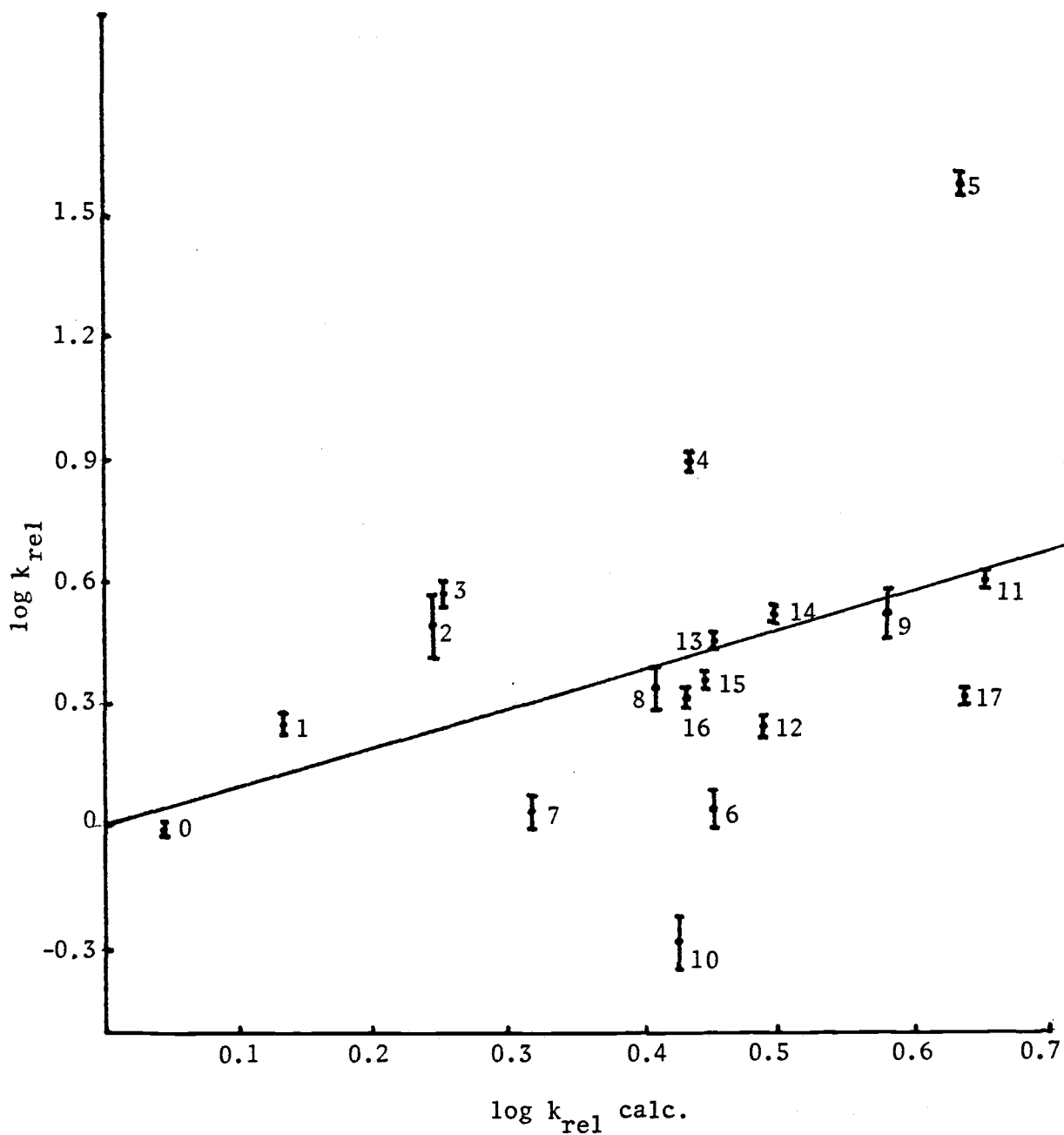


Figure 16. Logarithms of the relative rates of formation of homo and heteroarylmethyl radicals vs logarithms of the calculated rates using a four parameter equation ($\Delta\Delta E_{\pi \text{ radical}}$ and Δq).

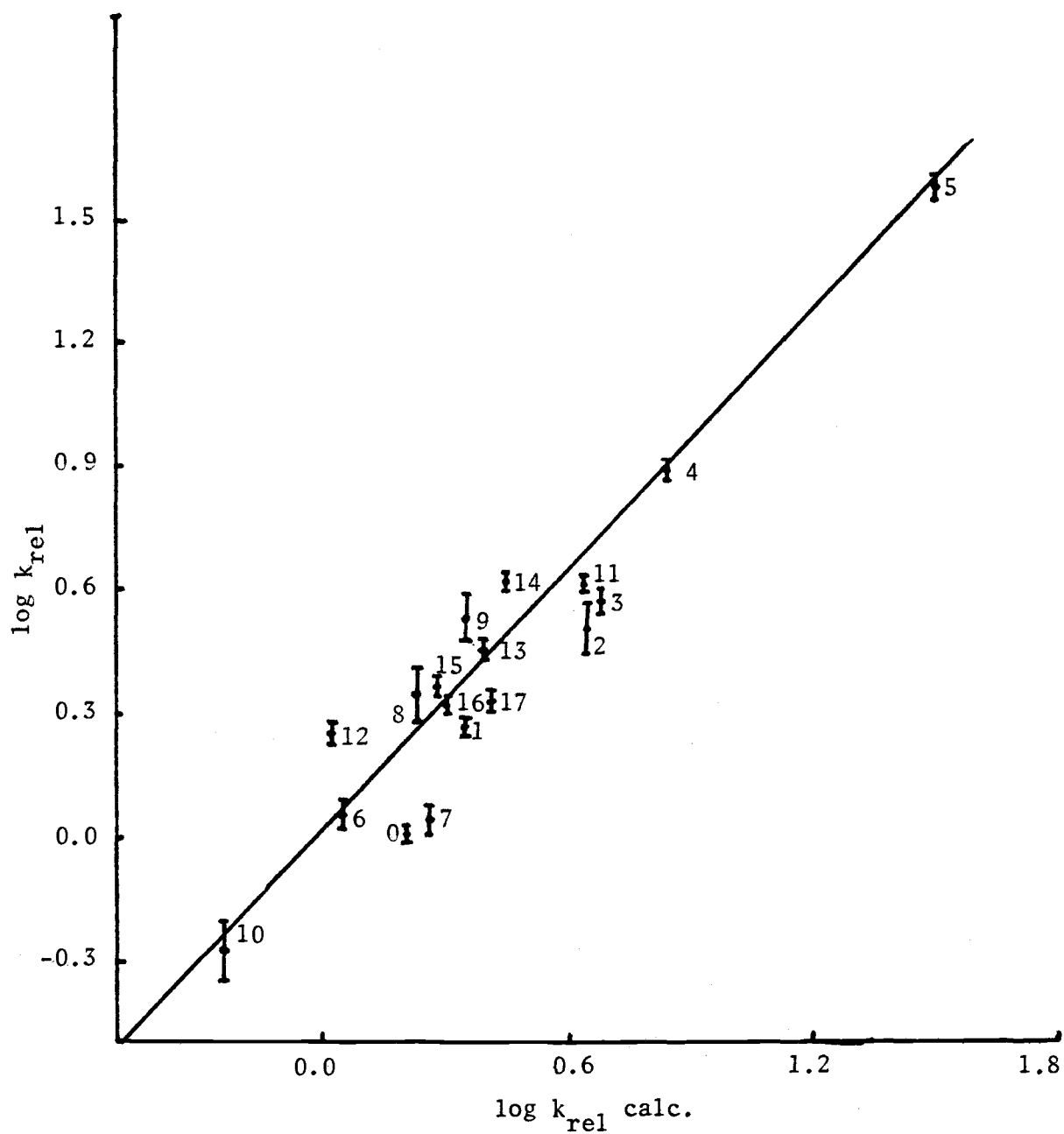


Figure 17. Logarithms of the relative rates of formation of homo and heteroarylmethyl anions vs logarithms of the calculated rates using a four parameter equation ($\Delta\Delta E_{\pi \text{ anion}}$ and Δq).

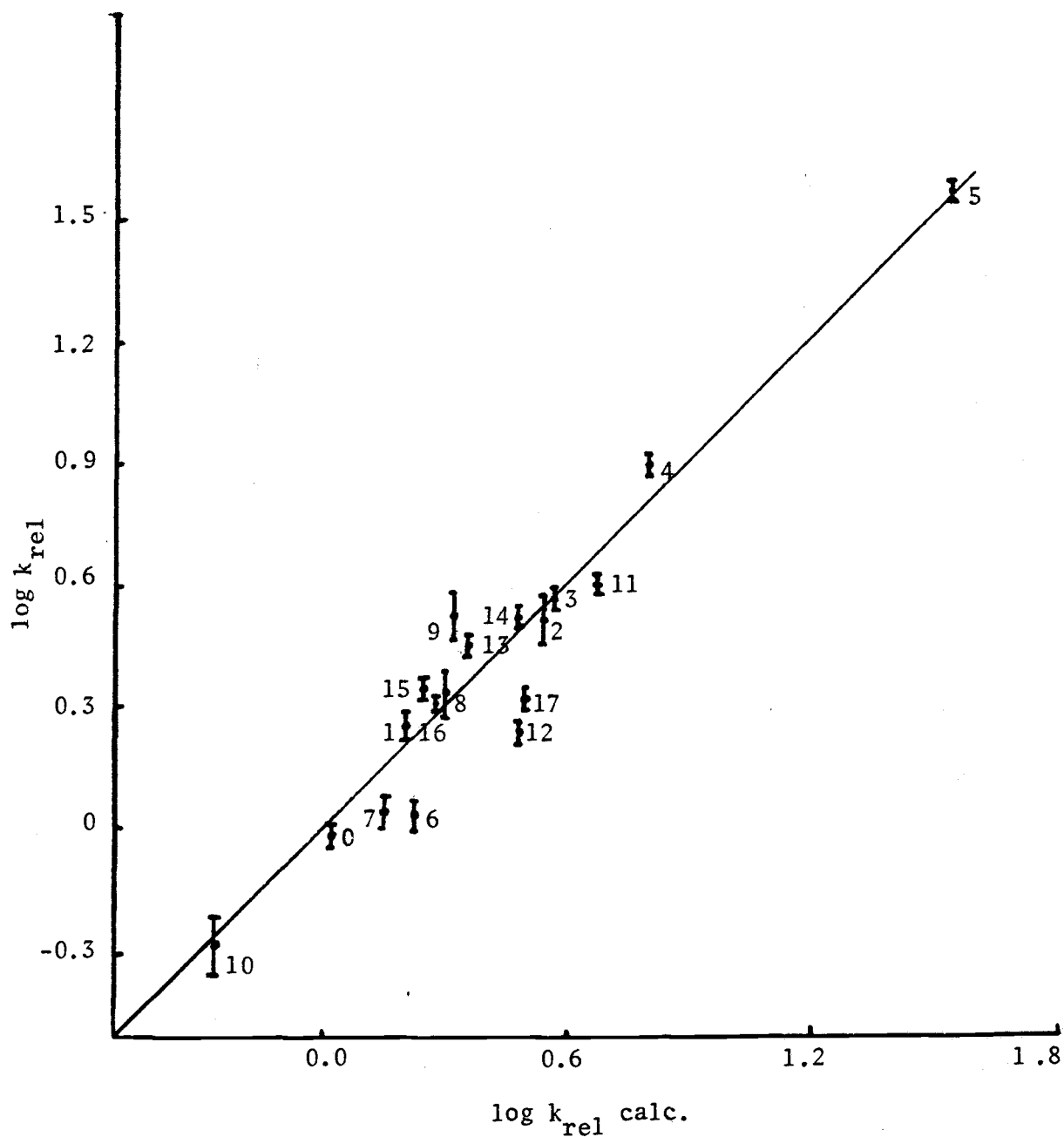


Figure 18. Logarithms of the relative rates of formation of homo and heteroarylmethyl intermediates vs logarithms of the calculated rates using a four parameter equation ($\Delta\Delta E_{\pi \text{ anion}}$ and $\Delta\Delta E_{\pi \text{ radical}}$).

double correlation to treat problems in heterocyclic reactivity has already been mentioned (36). It should be most fruitful for systems having relatively early transition states. Pryor has suggested that radical processes be generally so treated by a composite model with significant ground state contribution [52]. He cites several examples in justification. More recently, the correlation of some extremely rapid thiyl radical addition reactions have been treated by a combined transition state-ground state rationale [53]. Table 9 shows the value of the relative rates as calculated from four parameter equations. As might be expected, the poorest result is obtained from equation 35.

Table 9. Relative rates as calculated by various four parameter equations.

#	Molecule	k_{rel}^{exp}	$k_{rel}^{calc.}$			
			$\Delta\Delta E_{\pi}^{anion}$	$\Delta\Delta E_{\pi}^{radical}$	$\Delta\Delta E_{\pi}^{anion}^q$	$\Delta\Delta E_{\pi}^{radical}^q$
0	benzyl	1.00		1.06	1.60	1.12
1	2-naphthyl	1.88±0.11		1.61	2.25	1.36
2	1-naphthyl	3.29±0.48		3.56	4.54	1.77
3	9-phenanthryl	3.79±0.24		3.80	4.82	1.78
4	1-anthracyl	7.95±0.26		6.57	6.97	2.72
5	9-anthracyl	38.68±2.19		36.04	32.54	4.35
6	2-pyridyl	1.16±0.09		1.70	1.14	2.84
7	3-pyridyl	1.13±0.09		1.41	1.86	2.08
8	4-pyridyl	2.22±0.31		2.01	1.74	2.56
9	2-furanyl	3.45±0.45		2.15	2.27	3.81
10	3-furanyl	0.54±0.09		0.53	0.58	2.66
11	2-benzofuranyl	4.15±0.06		4.82	4.44	4.51
12	3-benzofuranyl	1.80±0.06		3.05	1.07	3.09
13	1-dibenzofuranyl	2.91±0.12		2.27	2.51	2.83
14	2-dibenzofuranyl	3.41±0.02		3.06	2.88	3.14
15	3-dibenzofuranyl	2.32±0.06		1.80	1.91	2.75
16	1-dibenzo(p)dioxinyl	2.09±0.05		1.92	2.10	2.71
17	2-dibenzo(p)dioxinyl	2.16±0.04		3.14	2.65	4.31
Average percent deviation				20%	21%	68%

EXPERIMENTAL

Procedures

Melting points were measured in unsealed capillary tubes with Büchi or Mel-temp melting points apparatus. Boiling points and melting points are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian A-60 or a Varian HA-100 instrument. Infrared spectra were taken on a Beckman IR 8, with the sample as a film between sodium chloride discs. A gas-liquid chromatograph equipped with a linear temperature programmer, a Sargent recorder with disc integration and thermal conductivity detectors was used for all the GLC analyses. Helium was used as the carrier gas, and a ten foot 5% SE 30 on chromosorb W column most frequently employed.

Purification of Reagents

Purification of benzene. Reagent grade benzene was washed with concentrated sulfuric acid, followed by distilled water and dried over magnesium sulfate. It was then distilled with approximately the first 20% of the distillate being discarded. The purified benzene was then stored over a large amount of sodium ribbon. Spectro grade benzene was used without further purification.

Purification of the internal standards. Commercial diphenylmethane or tert-butylbenzene was distilled. A constant boiling fraction was utilized, which contained no impurities by gas liquid chromatography analysis.

Purification of azobisisobutyronitrile. Commercially available AIBN was recrystallized from methanol and dried in a vacuum dessicator over

phosphorus pentoxide. Samples were kept under refrigeration until use.

Purification of Parent Arenes and Heteroarenes used in Kinetic Experiments. Anthracene, 9,10-dimethylantracene, pyridine, γ -picoline and furan were commercially available and were distilled just before utilization.

Preparation of the Compounds

Synthesis of triphenyltin hydride. The method of Hoyte and Denney was used [54]. A three neck flask fitted with a nitrogen tube inlet, a dropping funnel and a stirrer is charged with 150 ml of anhydrous ether at 0° C. Lithium aluminum hydride (1.56 g, 40.9 mmoles) is added and then triphenyltin chloride (38.5 g, 100 mmoles) is introduced. The mixture is stirred at the ice bath temperature for fifteen minutes and then at room temperature for three hours. The reaction mixture is slowly hydrolyzed with 100 ml of water with cooling in an ice water bath. The ether layer is separated and washed twice with 100 ml of ice water and then dried over magnesium sulfate. The ether is distilled off and the hydride distilled rapidly using an oil bath preheated to 200° C to give 31.8 g (90%) of the pure hydride m. p. 26° C lit 26-27° C, b. p. 162-168° C.

Synthesis of the alcohols. The pyridyl carbinols, 2-tetrahydrofurfuryl alcohol and 3-furfuryl alcohol were commercially available.

Preparation of 2-naphthyl, 9-phenanthryl and 9-anthracyl carbinols. A general procedure reported by Bachman [55] was used for the preparation of the carboxylic acids. A mixture of 0.15 mole of the bromoarene, 3.9 g of magnesium ribbon, 0.3 of iodine, 90 ml of ether and 90 ml of benzene was refluxed on a steam bath for four to five hours. The reaction

mixture was kept under an atmosphere of nitrogen. The Grignard reagent was carbonated and the resultant acid reduced by lithium aluminum hydride to the corresponding carbinol.

2-naphthyl carbinol 60% yield m. p. 78-79° C lit 80° C [56]

9-phenanthryl carbinol 70% yield m. p. 149°C lit 149-149.5° C [55]

9-anthracyl carbinol 80% yield m. p. 162.5° C lit 162-164° C [54]

Preparation of 1-anthracyl carbinol. Benzanthrone (30 g, 0.125 mole) was boiled with excess aqueous sulfuric acid, and chromium trioxide (five fold excess) was added in small portions for three and one-half hours [58]. This mixture was diluted with hot water. On cooling crystals of anthraquinone-1-carboxylic acid 29.2 g, 93% formed. The crude acid was then reduced by a suspension of zinc dust (60 g, 0.825 mole) in aqueous ammonia. After six hours of refluxing 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. 245-250° C lit 245° C [40]. The latter compound (8 g, 32 mmoles) in 200 ml of tetrahydrofuran was added to 4.2 g of lithium aluminum hydride in a little tetrahydrofuran (50 g, 0.52 mole). The mixture after six hours of refluxing was worked up as usual. The crude alcohol yield was 60% m. p. 110-120° C lit 125-126° C.

Preparation of furfuryl alcohol. Purified furfural was reduced by the Cannizzaro reaction. The alcohol was prepared by adding furfural (50 g, 0.52 mole) to a solution of 12.5 g of sodium hydroxide in 25 ml of water, keeping the reaction temperature around 20° C. After one hour the reaction mixture was extracted with ether. The ethereal extract was dried

and evaporated. The residue was distilled under reduced pressure and the furfuryl alcohol, a very pale yellow liquid, was collected at 77° C/15 mm. The pure product weighs 15 g, 29% yield.

Preparation of 2-benzofuranyl carbinol. Commercial coumarin (75 g, 0.5 mole) was reacted with bromine (80 g, 0.5 mole) in chloroform to give coumarin dibromide (106 g) 70% yield, m. p. 103.5° C lit 102-105° C [42]. The dibromide (100 g, 0.32 mole) was then added in small portions to an alcoholic solution of 4 moles of potassium hydroxide as to maintain the reaction mixture below 20° C. After the addition, the mixture was refluxed for thirty minutes and concentrated. The residue was diluted with ice water and acidified with a 6 N hydrochloric acid solution. The crude coumarilic acid, which precipitate was filtered and crystallized from a 50/50 mixture of ethanol and water. The coumarilic acid is colorless and weighs 40 g m. p. 190-193° C. The acid (32.4 g) was reduced by lithium aluminum hydride (12.3 g) in 350 ml of ether. The alcohol was isolated in 85% yield b. p. 112-115° C/1.1 mm lit 112-113° C/1.1 mm [59].

Preparation of benzofuranyl carbinol. Salicylaldehyde (106 g, 1 mole) was reacted with chloroacetic acid (94.5 g) in the presence of sodium acetate (80 g, 2 moles) in a 50/50 mixture of acetic acid and acetic anhydride (90 g, 0.5 mole). After work up, 95 g of benzofuran were obtained b. p. 98° C lit 97.5-99° C [59]. A solution of 62 g of bromine in CS₂ was added to 45 g of benzofuran in carbon disulfide cooled to -15° C. At the end of the addition, the solvent was distilled off under reduced pressure and the residue was used without further purification. The dibromide (28 g) was added with cooling in three to four portions to an alcoholic solution of potassium hydroxide as reported by Stoermer and

Kahlert [60]. After two hours of heating on a steam bath and steam distillation, the 3-bromobenzofuran was separated in 77% yield m. p. 39° C lit 38-39° C. The 3-bromobenzofuran (15 g) reacted with cuprous cyanide (8.26 g) in 17 ml of pyridine for 18 hours at 220° C. The reaction mixture was then extracted with a mixture of ammonium hydroxide and benzene. The benzene extract was washed with ammonium hydroxide, hydrochloric acid and finally, with water. The benzene was evaporated and the residue steam distilled to give 9 g of 3-cyanobenzofuran 84% m. p. 93° C lit 93° C [43]. The cyano compound (8 g) was hydrolyzed by a 20% solution of potassium hydroxide to the corresponding acid. This was in turn reduced in the usual manner by lithium aluminum hydride to the 3-benzofuranyl carbinol 80% yield b. p. 135-140° C/5mm.

Preparation of 1-dibenzofuranyl carbinol. The method of Gilman [61] was used to prepare the 1-dibenzofuranyl carboxylic acid. Dibenzofuran (15.2 g) was dissolved in 100 ml of THF. This solution was added over a period of forty-five minutes to 182 ml of 1.34 molar n-butyl lithium solution in ether. The reaction mixture was stirred at room temperature for five hours. After carbonation, the acid was isolated in 68% yield m. p. 210-212° C lit 211-213° C. The acid was then reduced to the corresponding alcohol in 82% yield by lithium aluminum hydride.

Preparation of 2-dibenzofuranyl carbinol. The method of Borsche and Bothe [41] was used to prepare the 2-benzofuranyl carboxylic acid. Dibenzofuran (42 g, 0.25 mole) in acetic acid 120 ml was nitrated with 38 ml of fuming nitric acid at 62° C. The heavy yellow precipitate of 2-nitrodibenzofuran was recrystallized from ethanol to give 40 g, 75.8% of pure product m. p. 180.5-183° C lit 181-182° C. The 2-nitrodibenzofuran

(30 g) was reduced by 60 g of granulated tin in hydrochloric acid to the corresponding amine m. p. 94° C. The amine (15 g) was diazotized and converted to the 2-cyano compound by reaction with cuprous cyanide. The cyano compound (8 g) was hydrolyzed to the carboxylic acid (7 g) by a refluxing with a 20% solution of potassium hydroxide. As usual, 6 g of the acid were reduced to the alcohol by lithium aluminum hydride in 75% yield.

Preparation of 1-dibenzo-p-dioxinyl carbinol. Dibenzo-p-dioxin was synthesized by the method of Gilman e. al. [62]. 2-chlorophenol (100 g, 0.77 mole), anhydrous potassium carbonate (54 g, 0.39 mole) and 6.24 g of copper sulfate was heated at 175° C for six hours. The dark reaction mixture was heated two more hours with aqueous potassium hydroxide. The cold mixture was extracted with ether. The ethereal solution was extracted with potassium hydroxide to dispell the color. Evaporation of the ethereal extract gave 23.1 g of crude dibenzo-p-dioxin 15% yield.

Dibenzo-p-dioxin (23 g, 0.12 mole) was added to a solution of 0.05 mole of n-butyl lithium in 300 ml of ether. The mixture was stirred for six hours and carbonated to give the 1-dibenzo-p-dioxinyl carboxylic acid (8 g) m. p. 208. The latter compound (6 g, 0.026 mole) was reduced with lithium aluminum hydride in the usual manner to the corresponding alcohol.

Synthesis of the aryl and heteroarylmethyl chlorides. Benzyl chloride, 1-chloromethylnaphthalene and neophyl chloride were commercially available. Because of the expected lability of all benzylic type halides, these compounds were prepared and/or purified just prior to use.

Preparation of the methylchlorides from the corresponding carbinols.

Method A: The carbinol was added to an excess of thionyl chloride in toluene and cooled in an ice bath. The mixture was slowly heated and

finally refluxed for one hour. The excess reagent and toluene were removed by evaporation and the residue distilled in vacuo to give pure arylmethyl chlorides as shown by the NMR spectra. The benzylic absorption of the alcohol is replaced by a new absorption with closed by, but different chemical shifts as shown in Table 10. The purity of the compounds was also checked by the infrared spectra, complete disappearance of the alcohol (O-H) absorption ($3650-3400\text{ cm}^{-1}$) was noted in all cases.

Method B: This method was used for the preparation of 2- and 3-chloromethylfuran and 2-chloromethyltetrahydrofuran. The first two chlorides have been reported [63] to be extremely unstable and potentially explosive. The general method reported by Kirner [64] was used. A mixture of the furfuryl alcohol and absolute ether was cooled in an ice bath and the solution was stirred. When the temperature fell to -10° C , a solution of purified thionyl chloride in pentane was added as rapidly as possible. The reaction temperature was always kept below 30° C . The addition was complete after fifteen minutes. The reaction mixture was worked up and the solvent removed. The residue was distilled under a reduced pressure of nitrogen to give the pure product.

Table 10. Chemical shifts of benzylic protons of the alcohols and chlorides employed in this study.

Compounds	$\delta\text{CH}_2\text{OH}$	$\delta\text{CH}_2\text{Cl}$
phenyl		4.51
1-naphthyl		5.00
2-naphthyl	4.82	4.73
1-anthracyl	5.63	5.55
9-anthracyl	5.63	5.53
9-phenanthryl	4.17	5.13
2-pyridyl	4.74	4.55
3-pyridyl	4.70	4.22
4-pyridyl	4.70	4.23
2-furanyl	4.50	4.98
3-furanyl		4.83
2-benzofuranyl		4.63
3-benzofuranyl		4.48
1-dibenzofuranyl		4.75
2-dibenzofuranyl		4.61
3-dubenzofuranyl		4.71
1-dibenzo-p-dioxinyl		4.57
2-dibenzo-p-dioxinyl		4.61

Preparation of 3-chloromethyldibenzofuran and 4-chloromethylphenyl

ether. To a solution of the parent arene (0.125 mole) in petroleum ether (b. p. 75-115° C) was added 6.2 g of trioxane and 5 g of zinc chloride. Gaseous hydrogen chloride was passed at a rapid rate into the stirred suspension through a tube extending to the bottom of the flask. After fifteen to twenty minutes, the color of the reaction mixture darkened and the temperature began to rise. The temperature was held at 55-60° C for one hour. The reaction mixture was poured into ice. The organic layer was separated and washed with ammonium hydroxide, hydrochloric acid, sodium bicarbonate and finally, water. The ether was removed by distillation and the chloride distilled under vacuo to give the pure chloride

3-chloromethyldibenzofuran 40% yield m. p. 78-79° C b. p. 160° C/3mm
lit 160°C/3mm (65)

4-chloromethylphenyl ether 50% yield m. p. 145° C.

Preparation of 2-chloromethyldibenzo-p-dioxin. A mixture of 9.2 g, 0.05 mole of dibenzo-p-dioxin, 4 g of paraformaldehyde, 50 ml of glacial acetic acid, 40 ml of concentrate hydrochloric acid and 15 ml of 85% phosphoric acid was heated at 80° C for twelve hours with mechanical stirring. Dilution of the reaction mixture with water followed by suction filtration produced 10.7 g of crude material. Vacuo distillation of the residue gave 34% of pure product m. p. 112.5° C lit 111-113° C.

Determination of the relative rate of chlorine abstraction. Solutions of two arylmethylchlorides, internal standard (diphenylmethane or t-butylbenzene), azobisisobutyronitrile and benzene were prepared in approximate molar ratio 1:1:1:0.1:100, and distributed into ampoules. A small amount of the mixture was reserved for analysis of the starting

material. The ampoules were frozen in an acetone-dry ice slurry as soon as possible. A solution of triphenyltin hydride and benzene in the approximate molar ratio of 1:12.5 was prepared and added to the above samples. The ampoules were then sealed under a reduced pressure of nitrogen and were placed in a constant temperature bath maintained at 70.0 ± 0.2 C for times varying from one to four hours. After completion of the reaction, the ampoules were opened and analyzed for the disappearance of the chloromethylarenes and the appearance of the arylmethanes via nuclear magnetic resonance using the aliphatic protons of diphenylmethane or *t*-butylbenzene as internal standards.

The procedure was to have the two arylmethylchlorides compete directly for the triphenyl tin radical. Benzyl chloride was the reference compound of choice. However, when one of the arylmethylchlorides was too reactive to compare directly with benzyl chloride, or when the benzylic protons in the two compounds overlapped, the reactivity was determined relative to some other arylmethylchloride. The value thus obtained was converted to the desired expression by using the following equation.

$$\left[\frac{k_x}{k_{\text{phenyl}}} \right]_{\text{dis}} = \left[\frac{k_y}{k_x} \right]_{\text{dis}} \cdot \left[\frac{k_x}{k_{\text{phenyl}}} \right]_{\text{dis}} \quad (38)$$

The relative rate constants of disappearance were obtained using the usual competitive procedure shown in equation 38.

$$\left(\frac{k_X}{k_M} \right)_{\text{dis}} = \frac{(\log X_o/X_f)}{(\log M_o/M_f)} \quad (39)$$

$\frac{k_X}{k_M}$ is the relative rate constant for the disappearance of a chloromethylarene relative to benzyl chloride. X_0 and M_0 are the number of mmoles originally present in the chloromethylarene and benzyl chloride. X_f and M_f are the corresponding terms for the final number of mmoles present. The absolute ratios were obtained directly from nuclear magnetic resonance spectra of the reaction mixture using the integrated areas of the benzylic proton signals.

$$\frac{x_0}{x_f} = \frac{\left[\frac{\text{area of X CH}_2 \text{ peak}}{\text{area of I CH}_2 \text{ peak}} \right] \text{ initially}}{\left[\frac{\text{area of X CH}_2 \text{ peak}}{\text{area of I CH}_2 \text{ peak}} \right] \text{ finally}} \quad (40)$$

Internal standard is represented by I. Tables 11 to 31 in the appendix give detailed data on the relative rates of disappearance of the chloromethylarenes.

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APPENDIX

Table 11. Relative rates of disappearance of neophyl chloride vs benzyl chloride.

Conditions:	4 hours at 70° C
Mmoles $(C_6H_5)_3SnH$	5.916
Mmoles AIBN	0.643
Mmoles $(C_6H_5)_2CH_2$	6.464
Mmoles C_6H_6	112.47

Run #	Compounds	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ neophyl}}{k \text{ benzyl}}$
1	neophyl	6.541	5.179	1.362	20.816	0.134
	benzyl	6.870	1.215	5.656	82.309	
2	neophyl	6.541	4.277	2.264	34.615	0.169
	benzyl	6.870	0.555	6.316	91.916	
3	neophyl	6.541	4.575	1.966	30.057	0.122
	benzyl	6.870	0.364	6.506	94.701	
4	neophyl	6.541	4.765	1.776	27.143	0.117
	benzyl	6.870	0.455	6.415	93.377	
5	neophyl	6.541	5.272	1.168	17.863	0.143
	benzyl	6.870	1.743	5.127	74.622	

The average $\frac{k \text{ neophyl}}{k \text{ benzyl}}$ is 0.134 ± 0.021

Table 12. Relative rates of disappearance of 2-chloromethylnaphthalene vs benzyl chloride.

Conditions: 3 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 6.346
 Mmoles AIBN 0.584
 Mmoles $(C_6H_5)_2CH_2$ 6.484
 Mmoles C_6H_6 112.47

Run #	Compounds	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 2-naphthyl}}{k \text{ phenyl}}$
1	2-naphthyl	6.934	1.389	5.545	79.968	1.917
	phenyl	6.451	2.788	3.663	56.773	
2	2-naphthyl	6.934	3.806	3.128	45.098	2.014
	phenyl	6.451	4.789	1.662	25.749	
3	2-naphthyl	6.934	2.175	4.758	68.632	2.003
	phenyl	6.451	3.615	2.836	43.949	
4	2-naphthyl	6.934	3.276	3.658	52.741	1.961
	phenyl	6.451	4.401	2.050	31.767	
5	2-naphthyl	6.934	2.757	4.177	60.275	1.797
	phenyl	6.451	3.861	2.590	40.138	
6	2-naphthyl	6.934	1.898	5.036	72.615	1.678
	phenyl	6.451	2.981	3.470	53.787	
7	2-naphthyl	6.932	3.381	3.553	51.229	1.781
	phenyl	6.451	4.310	2.141	33.180	

The average $\frac{k \text{ 2-naphthyl}}{k \text{ phenyl}}$ is 1.88 ± 0.11

Table 13. Relative rates of disappearance of 1-chloromethylnaphthalene vs benzyl chloride.

Conditions: 3 hours at 70° C
 Mmoles $(C_6H_5)_3Sn$ 6.340
 Mmoles AIBN 0.700
 Mmoles $(C_6H_5)_2CH_2$ 6.577
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 1-naphthyl}}{k \text{ phenyl}}$
1	1-naphthyl	5.420	1.063	4.357	80.383	3.813
	phenyl	6.426	4.192	2.234	34.769	
2	1-naphthyl	5.420	1.125	4.295	79.243	3.473
	phenyl	6.426	4.086	2.340	36.406	
3	1-naphthyl	5.420	1.513	3.097	72.074	3.588
	phenyl	6.426	4.503	1.923	29.921	
4	1-naphthyl	5.420	1.675	3.745	69.087	2.978
	phenyl	6.426	4.332	2.094	32.581	
5	1-naphthyl	5.420	0.613	4.807	88.689	2.620
	phenyl	6.426	2.792	3.634	56.473	
6	1-naphthyl	5.420	2.655	2.765	67.157	3.997
	phenyl	6.426	5.375	1.051	51.021	
7	1-naphthyl	5.420	1.780	3.640	67.157	2.560
	phenyl	6.426	4.156	2.270	35.266	

The average $\frac{k \text{ 1-naphthyl}}{k \text{ phenyl}}$ is 3.29 ± 0.48

Table 14. Relative rates of disappearance of 9-chloromethylphenanthrene vs benzyl chloride.

Conditions: 1:30 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 3.170
 Mmoles AIBN 0.347
 Mmoles $(C_6H_5)_2CH_2$ 3.529
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 9-phenanthryl}}{k \text{ phenyl}}$
1	9-phenanthryl	4.437	3.550	0.937	21.102	3.770
	phenyl	3.336	3.133	0.203	6.093	
2	9-phenanthryl	4.437	3.999	0.438	9.858	3.249
	phenyl	3.336	3.231	0.105	3.142	
3	9-phenanthryl	4.347	2.658	1.778	40.097	3.863
	phenyl	3.336	2.922	0.414	12.124	
4	9-phenanthryl	4.437	2.345	2.092	47.133	4.107
	phenyl	3.336	2.856	0.480	14.376	
5	9-phenanthryl	4.437	2.425	2.012	45.327	4.120
	phenyl	3.336	2.881	0.455	13.632	
6	9-phenanthryl	4.437	2.804	1.633	36.802	3.632
	phenyl	3.336	2.940	0.396	11.869	

The average $\frac{k \text{ 9-phenanthryl}}{k \text{ phenyl}}$ is 3.79 ± 0.24

Table 15. Relative rates of disappearance of 1-chloromethylantracene vs benzyl chloride.

Conditions: 3 hours at 70° C
 MMoles $(C_6H_5)_3SnH$ 6.347
 Mmoles AIBN 0.599
 Mmoles $(C_6H_5)_2CH_2$ 6.810
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	%RX	Mmoles used	$\frac{k \text{ 1-anthracyl}}{k \text{ phenyl}}$
1	1-anthracyl	6.675	0.855	87.179	5.820	8.043
	phenyl	6.452	4.952	28.819	1.500	
2	1-anthracyl	6.675	1.862	72.109	4.813	7.277
	phenyl	6.452	5.413	16.093	1.039	
3	1-anthracyl	6.675	2.760	58.647	3.915	7.165
	phenyl	6.452	5.704	11.595	0.748	
4	1-anthracyl	6.675	0.951	85.744	5.724	5.770
	phenyl	6.452	4.603	28.654	1.849	
5	1-anthracyl	6.675	2.440	63.439	4.235	8.646
	phenyl	6.452	5.545	14.050	0.907	
6	1-anthracyl	6.675	1.298	80.558	5.377	7.546
	phenyl	6.452	5.193	19.518	1.258	

The average $\frac{k \text{ 1-anthracyl}}{k \text{ phenyl}}$ is 7.95 ± 0.26

Table 16. Relative rates of disappearance of 9-chloromethylantracene vs 1-chloromethylantracene.

Conditions: 1 hour at 70° C
 Mmoles $(C_6H_5)_3SnH$ 3.307
 Mmoles AIBN 0.299
 Mmoles $(C_6H_5)_2CH_2$ 3.708
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 9-anthracyl}}{k \text{ phenyl}}$
1	9-anthracyl	3.020	1.318	1.702	56.352	4.900
	1-anthracyl	2.747	2.319	0.428	15.566	
2	9-anthracyl	3.020	1.457	1.563	51.732	5.991
	1-anthracyl	2.747	2.432	0.316	11.447	
3	9-anthracyl	3.020	2.013	1.007	33.338	5.936
	1-anthracyl	2.747	2.565	0.182	6.604	
4	9-anthracyl	3.020	1.315	1.705	56.445	6.003
	1-anthracyl	2.747	2.391	0.356	12.932	
5	9-anthracyl	3.020	1.790	1.230	40.732	6.287
	1-anthracyl	2.747	2.527	0.220	7.984	
6	9-anthracyl	3.020	1.965	1.055	34.921	5.030
	1-anthracyl	2.747	2.522	0.225	8.187	
7	9-anthracyl	3.020	1.457	1.563	51.743	5.974
	1-anthracyl	2.747	2.431	0.316	11.483	

The average $\frac{k \text{ 9-anthracyl}}{k \text{ 1-anthracyl}}$ is 5.73 ± 0.43

Table 17. Relative rates of disappearance of 2-chloromethylpyridine vs benzyl chloride.

Conditions:	3 hours at 70° C
Mmoles $(C_6H_5)_3SnH$	6.523
Mmoles AIBN	0.832
Mmoles $(C_6H_5)_2CH_2$	6.977
Mmoles C_6H_6	112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 2-pyridyl}}{k \text{ phenyl}}$
1	2-pyridyl	7.780	4.990	2.790	35.812	1.323
	phenyl	7.300	5.220	1.879	28.480	
2	2-pyridyl	7.780	5.204	2.576	33.102	1.065
	phenyl	7.300	5.004	2.295	31.433	
3	2-pyridyl	7.780	6.138	1.642	21.102	1.066
	phenyl	7.300	5.844	1.456	19.933	
4	2-pyridyl	7.780	5.886	1.894	24.342	1.141
	phenyl	7.300	5.716	1.584	21.685	
5	2-pyridyl	7.780	3.514	2.736	54.826	1.113
	phenyl	7.300	3.574	3.726	51.040	
6	2-pyridyl	7.780	6.447	1.333	17.121	1.300
	phenyl	7.300	6.318	0.982	13.449	
7	2-pyridyl	7.780	2.686	5.094	65.478	1.113
	phenyl	7.300	2.806	4.494	61.552	

The average $\frac{k \text{ 2-pyridyl}}{k \text{ phenyl}}$ is 1.16 \pm 0.08

Table 18. Relative rates of disappearance of 3-chloromethylpyridine vs benzyl chloride

Conditions: 3 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 6.540
 Mmoles AIBN 0.732
 Mmoles $(C_6H_5)_2CH_2$ 6.577
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 3-pyridyl}}{k \text{ phenyl}}$
1	3-pyridyl	6.767	3.892	2.875	42.486	1.320
	phenyl	6.593	4.079	2.511	38.124	
2	3-pyridyl	6.767	3.517	3.243	48.017	1.346
	phenyl	6.593	4.054	2.539	38.504	
3	3-pyridyl	6.767	4.720	2.047	30.247	1.005
	phenyl	6.593	4.607	1.986	30.120	
4	3-pyridyl	6.767	4.136	2.631	38.873	1.133
	phenyl	6.593	4.269	2.324	35.247	
5	3-pyridyl	6.767	4.389	2.378	35.130	1.011
	phenyl	6.593	4.297	2.296	34.821	
6	3-pyridyl	6.767	2.647	4.120	60.348	1.130
	phenyl	6.593	2.907	3.686	55.904	

The average $\frac{k \text{ 3-pyridyl}}{k \text{ phenyl}}$ is 1.29 ± 0.08

Table 19. Relative rates of disappearance of 4-chloromethylpyridine vs benzyl chloride.

Conditions: 3 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 6.365
 Mmoles AIBN 0.720
 Mmoles $C_6H_5-C(CH_3)_2$ 2.021
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 4-pyridyl}}{k \text{ phenyl}}$
1	4-pyridyl	4.166	1.627	2.534	60.936	1.933
	phenyl	6.477	3.985	2.494	38.502	
2	4-pyridyl	4.166	1.781	2.385	57.246	2.038
	phenyl	6.477	4.268	2.209	34.095	
3	4-pyridyl	4.166	1.980	2.186	52.454	2.505
	phenyl	6.477	4.813	1.664	25.683	
4	4-pyridyl	4.166	2.369	1.797	43.183	2.043
	phenyl	6.477	4.913	1.564	24.134	
5	4-pyridyl	4.166	2.077	1.887	45.292	2.877
	phenyl	6.477	5.252	1.227	18.911	
6	4-pyridyl	4.166	3.486	0.680	16.312	1.955
	phenyl	6.477	5.913	0.564	8.707	

The average $\frac{k \text{ 4-pyridyl}}{k \text{ phenyl}}$ is 2.22 ± 0.31

Table 20. Relative rates of disappearance of 2-tetrahydrofuranly chloride vs benzyl chloride.

Conditions: 4 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 11.594
 Mmoles AIBN 1.456
 Mmoles $(C_6H_5)_2CH_2$ 12.240
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 2-THfuranyl}}{k \text{ phenyl}}$
1	2-TH furanyl	10.829	10.035	0.793	7.325	0.077
	phenyl	11.171	4.162	7.008	62.737	
2	2-TH furanyl	10.829	9.514	1.321	12.139	0.130
	phenyl	11.171	4.143	7.027	62.911	
3	2-TH furanyl	10.829	10.130	0.699	6.454	0.072
	phenyl	11.171	4.429	6.741	60.346	
4	2-TH furanyl	10.829	9.250	1.578	14.577	0.139
	phenyl	11.171	3.601	7.570	67.767	
5	2-TH furanyl	10.829	9.122	2.203	15.116	0.144
	phenyl	11.171	4.261	6.909	61.854	
6	2-TH furnayl	10.829	10.829	0.715	6.697	0.081
	phenyl	11.171	4.755	6.400	57.433	
7	2-TH furanyl	10.829	9.103	1.726	15.935	0.161
	phenyl	11.171	3.806	7.365	65.931	

The average $\frac{k \text{ 2-TH furanyl}}{k \text{ phenyl}}$ is 0.11 ± 0.03

Table 21. Relative rates of disappearance of 2-chloromethylfuran vs benzyl chloride.

Conditions: 3 hours at 70° C
 Mmoles C_6H_5SnH 5.756
 Mmoles AIBN 0.654
 Mmoles $C_6H_5-C(CH_3)_3$ 2.275
 Mmoles C_6H_5 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 2-furanyl}}{k \text{ phenyl}}$
1	2-furanyl	6.202	2.355	3.847	62.019	3.026
	phenyl	6.164	4.400	1.764	27.380	
2	2-furanyl	6.202	2.001	4.201	62.477	3.262
	phenyl	6.164	2.368	3.796	29.127	
3	2-furanyl	6.202	2.928	3.274	52.783	3.167
	phenyl	6.164	3.863	2.301	21.096	
4	2-furanyl	6.202	2.107	4.095	65.006	4.368
	phenyl	6.164	3.846	2.318	21.368	
5	2-furanyl	6.202	4.848	78.129	78.129	5.816
	phenyl	6.164	2.418	22.997	22.977	

The average $\frac{k \text{ 2-furanyl}}{k \text{ phenyl}}$ is 3.45 ± 0.45

Table 22. Relative rates of disappearance of 3-chloromethylfuran vs benzyl chloride.

Conditions: 3 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 5.987
 Mmoles AIBN 0.712
 Mmoles $C_6H_5-C(CH_3)_3$ 2.180
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 3-furanyl}}{k \text{ phenyl}}$
1	3-furanyl	6.440	4.117	2.322	36.064	0.585
	phenyl	6.502	3.027	3.474	53.434	
2	3-furanyl	6.440	5.455	0.984	15.286	0.434
	phenyl	6.502	4.436	2.065	31.765	
3	3-furanyl	6.440	5.447	0.992	15.409	0.491
	phenyl	6.502	4.624	1.877	28.883	
4	3-furanyl	6.440	4.081	2.358	36.629	0.580
	phenyl	6.502	2.960	3.541	54.464	
5	3-furanyl	6.440	4.161	2.278	35.375	0.763
	phenyl	6.502	3.668	2.833	43.579	
6	3-furanyl	6.440	5.146	1.293	20.091	0.043
	phenyl	6.502	3.857	2.644	40.666	

The average $\frac{k \text{ 3-furanyl}}{k \text{ phenyl}}$ is 0.54 ± 0.09

Table 23. Relative rates of disappearance of 2-chloromethylbenzofuran vs 1-chloromethylnaphthalene.

Conditions: 2 1/2 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 6.987
 Mmoles AIBN 0.653
 Mmoles $C_6H_5-C(CH_3)_3$ 2.432
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 2-benzofuranyl}}{k \text{ 1-naphthyl}}$
1	2-benzofuranyl	7.835	3.484	4.437	56.529	1.146
	1-naphthyl	4.404	2.171	2.233	50.707	
2	2-benzofuranyl	7.835	5.096	2.738	34.954	1.310
	1-naphthyl	4.404	3.171	1.232	27.978	
3	2-benzofuranyl	7.835	5.088	2.746	35.048	1.124
	1-naphthyl	4.404	3.000	1.403	31.874	
4	2-benzofuranyl	7.835	4.268	3.566	45.526	1.486
	1-naphthyl	4.404	2.926	1.477	33.558	
5	2-benzofuranyl	7.835	3.395	4.439	56.667	1.221
	1-naphthyl	4.404	2.218	2.185	49.619	
6	2-benzofuranyl	7.832	3.875	3.959	50.533	1.324
	1-naphthyl	4.404	2.474	1.929	43.809	
7	2-benzofuranyl	7.832	4.907	2.927	37.369	1.221
	1-naphthyl	4.404	3.907	1.311	29.768	

The average $\frac{k \text{ 2-benzofuranyl}}{k \text{ 1-naphthyl}}$ is 1.26 ± 0.06

Table 24. Relative rates of disappearance of 3-chloromethylbenzofuran vs 1-chloromethylnaphthalene.

Conditions: 2 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 3.008
 Mmoles AIBN 0.457
 Mmoles $C_6H_5-C(CH_3)_3$ 3.127
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 3-benzofuranyl}}{k \text{ 1-naphthyl}}$
1	3-benzofuranyl	3.274	0.796	1.495	75.658	0.560
	1-naphthyl	2.986	0.238	2.550	91.996	
2	3-benzofuranyl	3.274	1.006	1.217	69.246	0.654
	1-naphthyl	2.986	0.492	2.197	83.501	
3	3-benzofuranyl	3.274	1.572	0.781	51.979	0.990
	1-naphthyl	2.986	1.423	2.129	52.317	
4	3-benzofuranyl	3.274	0.984	1.651	69.915	0.490
	1-naphthyl	2.986	0.256	2.660	91.395	
5	3-benzofuranyl	3.274	0.788	1.448	75.916	0.490
	1-naphthyl	2.986	0.163	2.511	94.540	

The average $\frac{k \text{ 3-benzofuranyl}}{k \text{ 1-naphthyl}}$ is 0.54 \pm 0.05

Table 25. Relative rates of disappearance of 1-chloromethyldibenzofuran vs 1-chloromethylnaphthalene.

Conditions: 3 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 6.502
 Mmoles AIBN 0.653
 Mmoles $C_6H_5-C(CH_3)_3$ 2.140
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 1-dibenzo-furanyl}}{k \text{ 1-naphthyl}}$
1	1-dibenzofuranyl	6.400	2.765	3.634	56.794	0.987
	1-naphthyl	6.585	2.384	4.204	63.848	
2	1-dibenzofuranyl	6.400	2.314	4.086	63.848	1.066
	1-naphthyl	6.585	2.535	4.049	61.491	
3	1-dibenzofuranyl	6.400	2.187	4.212	65.815	0.808
	1-naphthyl	6.585	1.743	4.841	73.516	
4	1-dibenzofuranyl	6.400	2.497	3.902	60.969	0.765
	1-naphthyl	6.585	1.925	4.659	70.759	
5	1-dibenzofuranyl	6.400	3.542	2.857	44.643	0.707
	1-naphthyl	6.585	2.852	3.732	56.677	
6	1-dibenzofuranyl	6.400	1.417	4.982	77.857	0.983
	1-naphthyl	6.585	1.420	5.164	78.435	

The average $\frac{k \text{ 1-dibenzofuranyl}}{k \text{ 1-naphthyl}}$ is 0.88 \pm 0.12

Table 26. Relative rates of disappearance of 2-chloromethyldibenzofuran vs 1-chloromethylnaphthalene.

Conditions: 2 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 4.637
 Mmoles AIBN 0.634
 Mmoles $C_6H_5-C(CH_3)_3$ 2.234
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 2-dibenzo-furanyl}}{k \text{ 1-naphthyl}}$
1	2-dibenzofuranyl	3.551	1.025	2.525	71.111	1.029
	1-naphthyl	6.513	1.948	4.560	70.074	
2	2-dibenzofuranyl	3.551	1.339	2.126	62.293	1.084
	1-naphthyl	6.513	2.648	3.865	59.342	
3	2-dibenzofuranyl	3.551	1.266	2.284	64.347	0.992
	1-naphthyl	6.513	2.302	4.211	64.659	
4	2-dibenzofuranyl	3.551	1.666	1.884	53.067	1.038
	1-naphthyl	6.513	3.142	3.370	51.750	
5	2-dibenzofuranyl	3.551	1.253	2.297	64.698	1.242
	1-naphthyl	6.513	2.815	3.647	56.761	

The average $\frac{k \text{ 2-dibenzofuranyl}}{k \text{ 1-naphthyl}}$ is 1.03 ± 0.02

Table 27. Relative rates of disappearance of 3-chloromethyldibenzofuran vs 1-chloromethylnaphthalene.

Conditions: 3 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 6.455
 Mmoles AIBN 0.650
 Mmoles $C_6H_5-C(CH_3)_3$ 2.432
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 3-dibenzo-furanyl}}{k \text{ 1-naphthyl}}$
1	3-dibenzofuranly	5.416	1.933	3.482	64.302	0.797
	1-naphthyl	6.372	1.749	4.623	72.552	
2	3-dibenzofuranyl	5.416	1.310	4.105	75.807	0.778
	1-naphthyl	6.372	1.028	5.343	83.857	
3	3-dibenzofuranyl	5.416	1.704	3.711	68.521	0.677
	1-naphthyl	6.372	1.157	5.215	81.847	
4	3-dibenzofuranyl	5.416	1.487	3.928	72.543	0.720
	1-naphthyl	6.372	1.059	5.312	83.375	
5	3-dibenzofuranyl	5.416	1.305	4.110	75.892	0.629
	1-naphthyl	6.372	0.664	5.707	89.573	
6	3-dibenzofuranyl	5.416	1.338	4.077	75.289	0.596
	1-naphthyl	6.372	0.610	5.761	90.418	
7	3-dibenzofuranyl	5.416	2.012	3.403	62.841	0.729
	1-naphthyl	6.372	1.638	4.606	72.286	

The average $\frac{k \text{ 3-dibenzofuranyl}}{k \text{ 1-naphthyl}}$ is 0.70 ± 0.06

Table 28. Relative rates of disappearance of 4-chloromethyldiphenyl-ether vs 1-chloromethylnaphthalene.

Conditions: 3 hours at 70° C
 Mmoles $(C_6H_5)_2-SnH$ 6.732
 Mmoles AIBN 0.702
 Mmoles $C_6H_5-C-(CH_3)_3$ 2.241
 Mmoles C_6H_6 112.47

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ phenyl-ether}}{k \text{ 1-naphthyl}}$
1	phenylether	6.693	3.797	2.895	43.260	0.687
	1-naphthyl	6.753	2.959	3.792	56.164	
2	phenylether	6.693	3.478	3.214	48.024	0.742
	1-naphthyl	6.753	2.796	3.956	58.584	
3	phenylether	6.693	3.739	2.953	44.131	0.692
	1-naphthyl	6.753	2.910	3.842	56.900	
4	phenylether	6.693	4.221	2.471	36.925	0.683
	1-naphthyl	6.753	3.439	3.313	49.062	
5	phenylether	6.693	5.353	1.339	20.019	0.624
	1-naphthyl	6.753	4.720	2.031	30.089	
6	phenylether	6.693	3.758	2.934	43.839	0.801
	1-naphthyl	6.753	3.285	3.467	57.347	

The average $\frac{k \text{ phenylether}}{k \text{ 1-naphthyl}}$ is 0.70 ± 0.04

Table 29. Relative rates of disappearance of 1-chloromethyldibenzo-p-dioxin vs 1-chloromethylnaphthalene.

Conditions: 2 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 3.256
 Mmoles AIBN 0.301
 Mmoles $C_6H_5-C-(CH_3)_3$ 1.103
 Mmoles C_6H_6 84.35

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 1-dibenzo-p-dioxin}}{k \text{ 1-naphthyl}}$
1	1-dibenzo-p-dioxin	3.567	2.056	1.509	42.323	0.995
	1-naphthyl	3.308	1.902	1.405	42.481	
2	1-dibenzo-p-dioxin	3.567	2.697	0.868	24.358	0.534
	1-naphthyl	3.308	1.960	1.346	40.707	
3	1-dibenzo-p-dioxin	3.567	2.557	1.008	28.285	0.625
	1-naphthyl	3.308	1.941	1.365	41.275	
4	1-dibenzo-p-dioxin	3.567	2.046	1.519	42.610	0.625
	1-naphthyl	3.308	1.498	1.838	55.564	
5	1-dibenzo-p-dioxin	3.567	2.611	0.955	26.788	0.613
	1-naphthyl	3.308	1.987	1.319	39.879	
6	1-dibenzo-p-dioxin	3.567	0.955	2.610	73.198	0.717
	1-naphthyl	3.308	0.565	2.780	84.065	

The average $\frac{k \text{ 1-dibenzo-p-dioxin}}{k \text{ 1-naphthyl}}$ is 0.63 ± 0.05

Table 30. Relative rates of disappearance of 2-chloromethyldibenzo-p-dioxin vs 1-chloromethylnaphthalene.

Conditions: 2 hours at 70° C
 Mmoles $(C_6H_5)_3SnH$ 3.021
 Mmoles AIBN 0.320
 Mmoles $C_6H_5-C-(CH_3)_3$ 3.543

Run #	Compound	Mmoles initial	Mmoles final	Mmoles used	%RXN	$\frac{k \text{ 2-dibenzo-p-dioxin}}{k \text{ 1-naphthyl}}$
1	2-dibenzo-p-dioxinyl	3.729	1.165	2.044	54.837	0.756
	1-naphthyl	3.337	1.734	2.171	65.067	
2	2-dibenzo-p-dioxinyl	3.729	3.022	0.706	18.937	0.646
	1-naphthyl	3.337	2.411	0.925	27.744	
3	2-dibenzo-p-dioxinyl	3.729	2.666	1.062	28.489	0.630
	1-naphthyl	3.337	1.960	1.376	41.258	
4	2-dibenzo-p-dioxinyl	3.729	3.358	0.370	9.948	0.558
	1-naphthyl	3.337	2.765	0.571	17.116	
5	2-dibenzo-p-dioxinyl	3.729	2.283	1.445	38.761	0.655
	1-naphthyl	3.337	1.577	1.739	52.724	
6	2-dibenzo-p-dioxinyl	3.729	2.388	1.340	35.942	0.698
	1-naphthyl	3.337	1.762	1.574	47.193	

The average $\frac{k \text{ 2-dibenzo-p-dioxinyl}}{k \text{ 1-naphthyl}}$ is 0.65 ± 0.04 .

Table 31. Material balances of the kinetic runs.

Compounds	Material balance
neophylchloride vs benzyl chloride	89.17±17.39
1-chloromethylnaphthalene vs benzyl chloride	107.47± 6.45
2-chloromethylnaphthalene vs benzyl chloride	93.47± 8.34
1-chloromethylantracene vs benzyl chloride	99.54± 3.01
9-chloromethylphenanthrene vs benzyl chloride	81.90±12.39
9-chloromethylantracene vs 1-chloromethylantracene	82.04±16.18
2-chloromethylpyridine vs benzyl chloride	97.41± 4.70
3-chloromethylpyridine vs benzyl chloride	97.05±16.29
4-chloromethylpyridine vs benzyl chloride	104.39±20.63
2-chloromethyltetrahydrofuran vs benzyl chloride	undefined
2-chloromethylfuran vs benzyl chloride	113.31±13.02
3-chloromethylfuran vs benzyl chloride	90.24±24.53
1-chloromethyldibenzofuran vs 1-chloromethylnaphthalene	99.93± 0.120
2-chloromethyldibenzofuran vs 1-chloromethylnaphthalene	100.89± 1.2
3-chloromethyldibenzofuran vs 1-chloromethylnaphthalene	105.66±23.78
4-chloromethylphenylether vs 1-chloromethylnaphthalene	107.49±13.02
2-chloromethylbenzofuran vs 1-chloromethylnaphthalene	99.46±16.96
3-chloromethylbenzofuran vs 1-chloromethylnaphthalene	84.9 ±14.20
1-chloromethyldibenzo-p-dioxin vs 1-chloromethylnaphthalene	114.49±18.92
2-chloromethyldibenzo-p-dioxin vs 1-chloromethylnaphthalene	100.11± 0.26
The average material balance is 98.36 ± 9.51	