ABSTRACT

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Title: ATOM ABSTRACTION FROM EXOCYCLIC POSITIONS OF DERIVATIVES OF METHYLATED PYRIDINES AND QUINOLINES: AN EVALUATION OF CHARGE SEPARATION IN THE TRANSITION STATES OF THESE REACTIONS

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Gerald Jay Gleicher

The relative rates of hydrogen atom abstraction from a series of 13 homoaryl and heteroarylmethanes by the nucleophilic undecyl radical, thermally generated from lauroyl peroxide, were determined at 70 °C. A reactivity range of 15 was obtained. Substantial differences in reactivity among isomers were found. The relative reactivities of the compounds studied were correlated with SCF-PPP calculated energy differences. Modest correlation was obtained when a carbanion model was used for the transitions state (r = 0.88). Much poorer correlations were obtained when either a carbocation or radical was used to model the transition state. Best correlations were obtained when the logarithms of the relative rates of hydrogen atom abstraction are plotted against those for base catalyzed hydrogen-deuterium exchange (r = 0.91). These results are suggestive of substantial negative charge development in the transition state.

The free-radical reduction of all isomers of chloromethylpyridine and chloromethylquinoline with triphenyltin hydride at 70 °C was also investigated. Small differences in reactivity among isomers were found. A reactivity range of ca. 4.5 was obtained. This is much smaller than the reactivity range found for hydrogen atom abstraction from methylpyridines and methylquinolines by undecyl radical. This is rather surprising since Hammett studies suggest that the selectivities in these two systems should be at least comparable. It is felt that the rate determining step might involve an electron transfer rather than direct atom abstraction. Good results ($r = 0.94$) are obtained for correlation involving plotting the logarithms of the experimental relative rates against the logarithms of the corresponding calculated relative rates using a four parameter equation based on SCF relative LUMO energy differences of the parent unsubstituted systems and SCF total energy differences for a carbanion model.

Atom Abstraction from Exocyclic Positions of Derivatives of Methylated Pyridines and Quinolines: An Evaluation of Charge Separation in the Transition States of These Reactions

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TO MY PARENTS

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"Reasoning draws a conclusion and makes us grant the conclusion, but does not make the conclusion certain, nor does it remove doubt so that the mind may rest on the intuition of truth, unless the mind discovers it by the path of experience."

Roger Bacon

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ATOM ABSTRACTION FROM EXOCYCLIC POSITIONS OF DERIVATIVES OF METHYLATED PYRIDINES AND QUINOLINES: AN EVALUATION OF CHARGE SEPARATION IN THE TRANSITION STATES OF THESE REACTIONS

INTRODUCTION

The rates of free-radical reactions have long been known to be sensitive to the presence of polar substituents in the substrate.[1] This observation has been supported by recent findings.[2] Probably the most fruitful method for investigating the importance of polar effects in free-radical reactions has been the application of the Hammet sigma-rho equation.[3-6]

Since Walling and Mayo reported the first application of the Hammett equation to a free-radical reaction some 40 years ago,[7] polar effects in radical reactions, and in particular such effects in hydrogen atom transfer reactions from substituted toluenes, have been the object of an extensive study.[2,8,9] The early investigations of hydrogen atom abstraction from substituted toluenes showed that electron donating substituents enhanced the reactivity toward electrophilic abstracting agents such as halogen atoms,[6b,10,11] a variety of oxygen radicals[11,12] and certain carbon radicals.[13,14,15] Walling and Miller[16] suggested that the polar effect observed in the photochlorination of substituted toluenes could be rationalized in terms of polar resonance structures, and they recognized the need for two different sigma values for substituents capable of resonance interactions in the transition state.[16] Subsequently, Russell showed that a number of kinetic data taken from literature gave excellent correlation with sigma-plus substituent constants.[17]

The polar effect in hydrogen atom abstraction may be rationalized as the perturbation of the substituent on the polar contribution inherent in the transition

state. Therefore for an abstraction by a radical X with a greater electron affinity than carbon (electrophilic radical), the absolute value of rho should reflect the importance of canonical form III.

$$\underset{\mathrm{I}}{[ArCH_2{-}H\ \dot{X}} \longleftrightarrow \underset{\mathrm{II}}{Ar\dot{C}H_2\ H{-}X} \longleftrightarrow \underset{\mathrm{III}}{Ar\overset{+}{C}H_2\ \dot{H}\ \overset{-}{:}X]}$$

The same argument predicts that the correlation changes from sigma to sigma-plus in the Hammet relationship as the difference in the electronegativity between the substrate and the radical increases. Figure 1 illustrates the improvement in the Hammett correlation upon utilization of sigma-plus constants for hydrogen atom abstraction from substituted toluenes by the electrophilic bromine atom. Table 1 is a compilation of rho values for hydrogen atom abstraction from substituted toluenes by a variety of radicals and atoms.

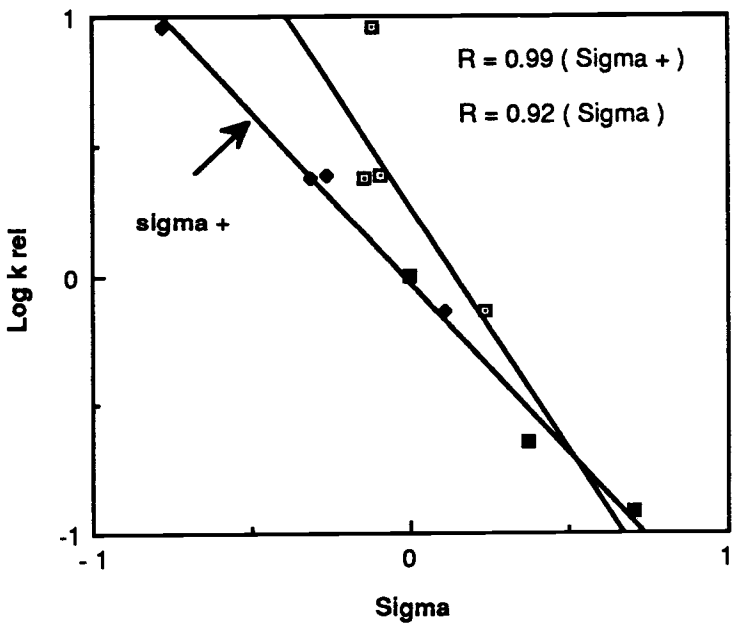


Figure 1. Hammett plot for bromination of substituted toluenes at 80 °C.

Table 1. Hydrogen Atom Abstraction from Substituted Toluenes.

Abstracting Species	T °C	ρ	σ or σ^+	Ref.
$H^\bullet$	40	-0.1	σ^*	23
$CH_3^\bullet$	100	-0.1	σ	15
$C_6H_5^\bullet$	60	-0.1	σ	14
$p\text{-}CH_3C_6H_4^\bullet$	60	-0.1	σ	20
$p\text{-}BrC_6H_4^\bullet$	60	-0.1	σ^+	20
$HO_2CCH_2^\bullet$	130	-0.7	σ^+	20
$p\text{-}NO_2C_6H_4^\bullet$	60	-0.6	σ^+	21
$Cl_3C^\bullet$ in C_6H_5Cl	50	-1.5	σ^+	13
$Cl^\bullet$ in CCl_4	40	-0.7	σ^+	6b
$Br^\bullet$ in CCl_4	80	-1.4	σ^+	10,18,19
$(CH_3)_2N^\bullet$	136	-1.1	σ^+	26
$(CH_3)_3CO^\bullet$	40	-0.4	σ^+	26
$(C_6H_5)_3CO^\bullet$	22	-1.1	σ^+	25
$(CH_3)_3COO^\bullet$	30	-0.6	σ^+	22

The somewhat low value of rho (-0.7) for hydrogen atom transfer from toluenes to chlorine atom is indicative of a low degree of bond breaking in the transition state. In the abstraction by bromine atom, which has an electron affinity similar to that of chlorine, the rho value is -1.4, indicative of extensive bond breaking in the transition state.

The magnitude of rho for hydrogen atom abstraction by polar species has been shown to decrease as the stability of the incipient radical increases. For example, the absolute value of rho for benzylic hydrogen atom abstraction by bromine atom decreases in going from substituted toluenes[10] to ethyl benzenes[27] to cumenes.[28] This is shown in Table 2.

Alkoxyl radicals have been extensively studied because of their importance in a variety of reactions. Kochi has reviewed the subject,[30] and Brun and Walgell have written a critical review on potential uses of alkoxyl radicals in synthetic organic reactions.[31] In this section, we will limit our discussion to hydrogen atom abstraction by tert-butoxyl radical.

The tert-butoxyl radical can be generated by the decomposition of tert-butyl hypohalites,[11,33-35] di-tert-butyl peroxalate,[11,12] di-tert-butyl hyponitrite,[11] and di-tert-butyl peroxide.[32,36-39] Hydrogen atom abstraction by tert-butoxyl radical has been widely investigated. Particular interest has been focused on substituted toluenes and possible application of the Hammett equation. Some of the results obtained are summarized in Table 3. Hydrogen atom abstraction from substituted benzaldehydes,[40] and α-heteroatom substituted toluenes[41] have also been investigated.

Early attempts to evaluate the rho value for side chain chlorination of substituted toluenes by tert-butyl hypochlorite led to controversial results. The originally proposed radical chain mechanism for this reaction is shown in Scheme 1. It utilizes tert-butoxyl radical as the chain carrying species.

Table 2. Rho Values for Benzylic Hydrogen Atom Abstraction from Substituted Aralkanes.

Substrates	T/°C	ρ(σ)	Ref.
	Bromine atom		
Toluenes	80 C_6H_6	-1.4 (σ^+)	10
Toluenes	80 CCl_4	-1.3 (σ^+)	18,19
Ethylbenzenes	80	-0.7 (σ^+)	27
Cumenes	70	-0.38 (σ)	28
Cumenes	70	-0.24 (σ^+)	28
	Trichloromethyl radical		
Toluenes	55	-1.5 (σ^+)	13
Ethylbenzenes	80	-0.5 (σ^+)	29
Cumenes	70	-0.89 (σ)	28
Cumenes	70	-0.67 (σ^+)	28
	Peroxyl radical		
Toluenes	30	-0.6 (σ^+)	22
Cumenes	30	-0.3 (σ)	22

Table 3. Rho Values for Hydrogen Atom Abstraction from Substituted Toluenes by *t*-Butoxyl Radical.

Source of *t*-butoxyl radical	T/°C	optimum (ρ)	Ref.
DTBP	110.0	-0.500 (σ)	32
TBHC	40.0	-0.830 (σ^+)	33
TBHC	39.6	-0.750 (σ^+)	34
TBHC	40.0	-0.680 (σ^+)	35
TBPO	40.0	-0.35 (σ^+)	12
TBPO	40.0	-0.32 (σ^+)	12
TBPO	40.0	-0.39 (σ^+)	12
TBHB	40.0	-0.401 (σ^+)	11
TBHN	40.0	-0.345 (σ^+)	11
TBHO	40.0	-0.345 (σ^+)	11

DTBP: di-*t*-butyl peroxide
TBHC: *t*-butyl hypochlorite
TBPO: di-*t*-butyl peroxalate
TBHB: *t*-butyl hypobromite
TBHN: di-*t*-butyl hyponitrite

Scheme 1

$$(CH_3)_3COCl \xrightarrow{In} (CH_3)_3CO^{\bullet} + InCl \qquad \text{eq. 1}$$

$$(CH_3)_3CO^{\bullet} + RH \xrightarrow{rds} (CH_3)_3CO + R^{\bullet} \qquad \text{eq. 2}$$

$$(CH_3)_3COCl + R^{\bullet} \longrightarrow RCl + (CH_3)_3CO^{\bullet} \qquad \text{eq. 3}$$

$$(CH_3)_3CO^{\bullet} \longrightarrow {}^{\bullet}CH_3 + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \qquad \text{eq. 4}$$

$$^{\bullet}CH_3 + (CH_3)_3COCl \longrightarrow CH_3Cl + (CH_3)_3CO^{\bullet} \qquad \text{eq. 5}$$

$$^{\bullet}CH_3 + RH \longrightarrow CH_4 + R^{\bullet} \qquad \text{eq. 6}$$

However, in a later report, Walling and McGuiness have shown that the cause for the controversy may be due to inclusion of chlorine atom in the chain-carrying process when tert-butyl hypochlorite is used.[11] Such inclusion is shown in Scheme 2.

The inclusion of chlorine atom in the chain carrying process is observed only when the incipient radical $R^{\bullet}$ formed in equations 2 and 8 is relatively unreactive. Thus, a stable radical, like benzyl, is selective enough to discriminate between chlorine atom abstraction from molecular chlorine or tert-butyl hypochlorite. It has been reported that reactions of benzylic radicals with molecular chlorine are low energy processes. Reaction with hypochlorite is much slower, and requires an appreciable activation energy.[33] Furthermore, Walling and McGuiness found that

Scheme 2

$$(CH_3)_3COCl \longrightarrow (CH_3)_3CO^{\bullet} + Cl^{\bullet} \qquad \text{eq. 7}$$

$$RH + Cl^{\bullet} \longrightarrow R^{\bullet} + HCl \qquad \text{eq. 8}$$

$$(CH_3)_3COCl + HCl \longrightarrow (CH_3)_3COH + Cl_2 \qquad \text{eq. 9}$$

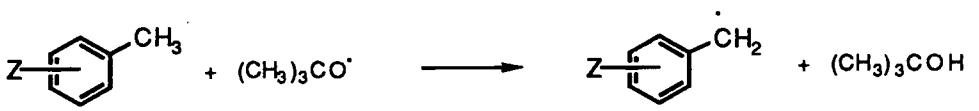
$$R^{\bullet} + Cl_2 \longrightarrow RCl + Cl^{\bullet} \qquad \text{eq. 10}$$

addition of trichloroethylene as a chlorine atom trap can efficiently stop this competing chain.[11] The relative rates they obtained for tert-butyl hypochlorite in the presence of trichloroethylene are now in good agreement with those reported by Sakurai for other sources of the tert-butoxyl radical.[12]

The selectivity of the tert-butoxyl radical was originally thought to be intermediate between those of chlorine and bromine atoms.[33] However, examination of the rho values for hydrogen atom abstraction by these radicals (Table 1) indicates that the tert-butoxyl radical is closer in selectivity to chlorine atom. The low rho value might be due to the lower electronegativity of the tert-butoxyl radical compared to that of chlorine atom,[6b] as well as a smaller amount of bond breaking in the transition state. The tert-butoxyl radical is more reactive than bromine atom or trichloromethyl radical as a hydrogen abstracting agent. Therefore, the transition state for hydrogen atom abstraction by this species should be relatively earlier than that found for bromine or trichloromethyl radical. This view should be substantiated by primary isotope effect measurements. In general, the transition state of hydrogen atom abstraction by extremely reactive atoms or radical involves little bond breaking

and exhibits a low primary deuterium isotope effect.[43,44] As the reactivity of the abstraction agent decreases, the deuterium isotope effect increases until it reaches a limit (k_H/k_D = 7 at 25 °C),[45] which corresponds to a symmetrical transition state with 50% bond breaking and making. Unfortunately recent measurements are not to be found in the literature. Early results yield data which are not always supportive of this picture.[14,44,46-48]

In the early 1970's, Zavitsas and Pinto, in a reexamination of hydrogen atom abstraction from substituted toluenes by tert-butoxyl radical (eq. 11) maintained that the postulation of partial charge separation in the transition state is unnecessary.[49]

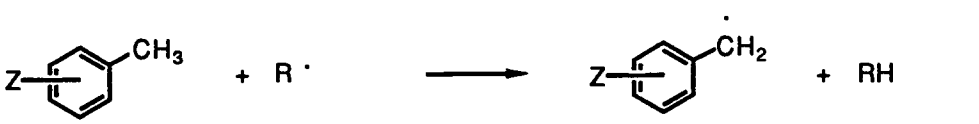


eq.11

They argued that the observed rate enhancement found for substrates containing electron donating groups was due solely to these groups' ability to weaken benzylic carbon hydrogen bonds.[49]

Subsequent studies did not substantiate that view. A consequence of the Zavitsas-Pinto argument is the prediction that only negative rho values should be observed in hydrogen atom abstraction from substituted toluenes.[49]

Several later investigations have reported positive rho values for hydrogen atom abstraction by alkyl radicals such as *t*-butyl,[50] i-propyl,[50b], 3-heptyl[51] and undecyl.[52] The rho values for hydrogen atom abstraction from substituted toluenes (eq. 12) by the aforementioned carbon radicals are summarized in Table 4.



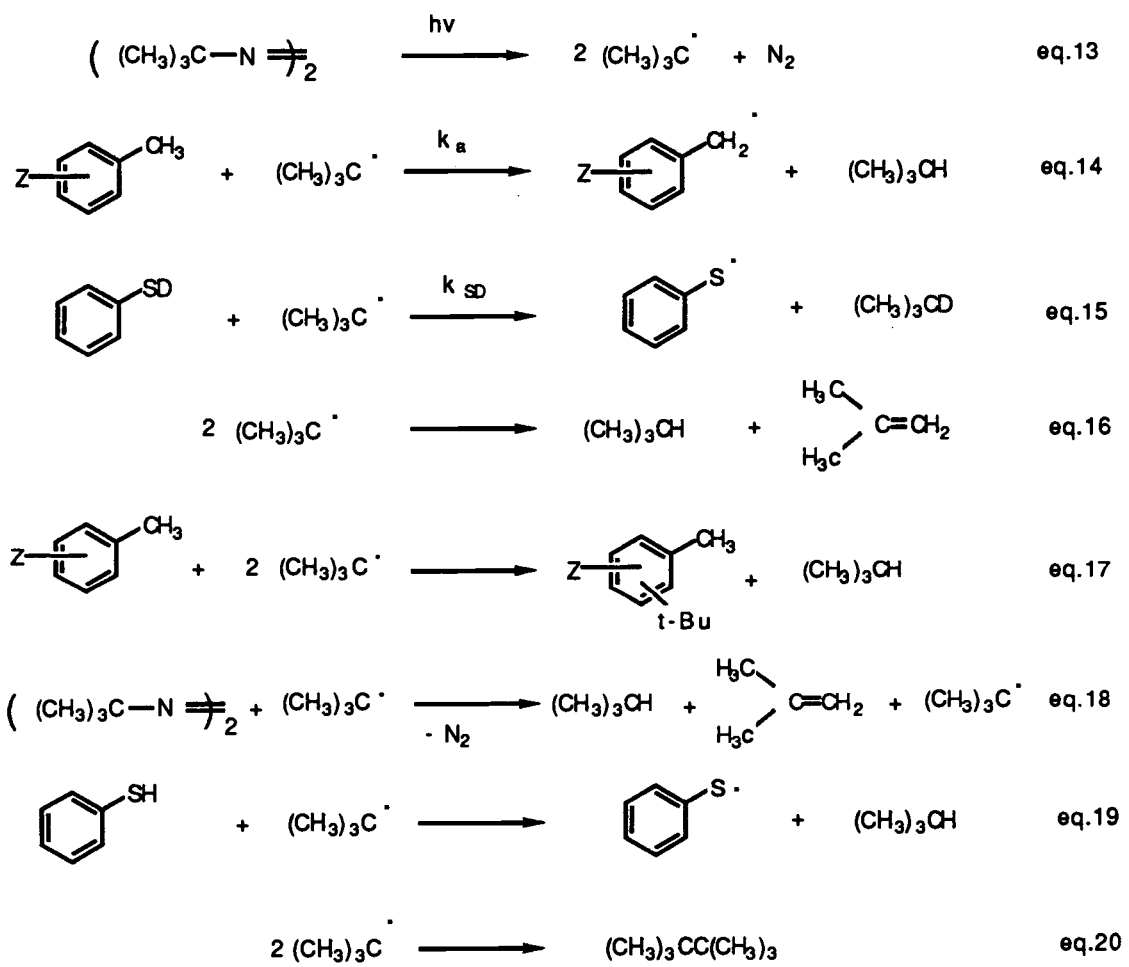
eq.12

Table 4. Rho Values for Hydrogen Atom Abstraction from Substituted Toluenes by Alkyl Radical.

Radical	T/°C	ρ	Ref.
Methyl	110	-0.02 ± 0.2	53
Isopropyl	30	-0.830	50b
3-Heptyl	80	-0.750	51
tert-Butyl	30	0.8 ± 0.1	50b
tert-Butyl	80	0.70 ± 0.09	50c
tert-Butyl	30	0.99 ± 0.04	50a
tert-Butyl	30	0.60	50d
tert-Butyl	48	0.59	54
Undecyl	80	0.45 ± 0.07	52a
Undecyl	81	0.50 ± 0.02	52b
Undecyl	81	0.40	52c

The first of these positive rho values was reported by Pryor and coworkers, who utilized the tert-butyl radical.[50a] It was generated by photolysis of 2,2'-azoisobutane (AIB) in a mixture of the substituted toluene and thiophenol-d at 30 °C. Thiophenol-d was used as a reference in determining the relative reactivities of the substituted toluenes studied. A mass spectroscopic method was used to determine the ratio of isobutane to isobutane-2-d formed during the course of the reaction as shown in Scheme 3.

Scheme 3



The mass spectroscopic analysis turned out to be difficult. The parent peaks (m/e 58 and 59) were found to be too small to be accurately measured. Instead, the intensities of M-15 peaks (m/e 43 and 44) were utilized to determine the ratio of isobutane to isobutane-2-d.[50a]

The relative rates (k_a/k_{SD}) should be equal to the slope of the plot of the ratio of mass 43 to 44 vs [QH]/[RSD] ratio of concentration of the hydrogen donor (QH) to that of thiophenol-d (RSD), providing that hydrogen atom abstraction from toluenes is the only important source for isobutane. Pryor and coworkers argued that all other sources for extraneous isobutane were negligible.[50a] The following points were made.

1 - Hydrogen atom abstraction from a constant amount of RSH impurity (eq. 19) should affect the intercept but not the slope of (m/e 43)/(m/e 44) vs [QH]/[RSD].[44]

2 - The induced decomposition of AIB does not take place, since thermolysis of azoisobutyronitrile (AIBN) or tert-butyl peroxypivalate (BPP) in a solution of toluene and AIB does not effect AIB concentration.

3 - Cage disproportionation of tert-butyl radical is negligible since AIB and BPP give the same results, and BPP cannot form isobutane within the cage.

4 - Disproportionation of tert-butyl radical in solution containing RSD should not take place.[55] The yield of the dimer (eq. 20) remains small and constant even as the thiol concentration is varied by 30-fold.

5 - Addition to the ring would yield isobutane (eq. 17), this possibility could be eliminated since no substituted methyl-tert-butylbenzenes were detected.

Correlation of the relative rates with sigma substituent parameters gave a rho value of 0.94 ± 0.04 at 30 °C with a correlation coefficient of 0.96.[50a] This was the first positive rho value for hydrogen atom transfer from toluenes.

Literature data on methyl radical[15,56] seem to indicate that hydrogen atom transfer from toluenes to the methyl radical is isoentropic. Furthermore, review of thermodynamic data also suggests that all atom transfer processes are isoentropic.[57] This led Pryor to conclude that the positive rho value has a mechanistic importance.

Polar effects in hydrogen atom transfer had been ascribed to the resonance stabilization of the transition state by polar structures such as III when X is an electrophilic radical.

$$[R{-}H\ {}^{\bullet}X \longleftrightarrow R^{\bullet}\ H{-}X \longleftrightarrow R^{+}\ H^{\bullet}\ {:}X^{-}]$$

I II III

Pryor's report of positive rho values for hydrogen atom abstraction from substituted toluenes by tert butyl radical[50a,b] led to an expansion of the resonance description of the transition state to four canonical forms shown below.[50a,b]

$$[R{-}H\ {}^{\bullet}X \longleftrightarrow R^{\bullet}\ H{-}X \longleftrightarrow R^{+}\ \overset{\bullet}{H}\ \overset{\bullet\bullet}{X}^{-} \longleftrightarrow R^{\bullet\bullet}\ \overset{\bullet}{H}\ X^{+}]$$

I II III IV

Resonance form IV is expected to make a large contribution to the hybrid description of the transition state of hydrogen atom abstraction when X is a nucleophilic radical.[50a,b]

Tanner, et al. in a later publication[50d] challenged the positive rho values reported by Pryor[50a,b] for hydrogen atom abstraction from toluenes by carbon

radicals. Probably the most important point in Tanner's evaluation of Pryor's kinetic analysis is[50a] that the assumption that the benzylic position of the substituted toluenes investigated was the only source of hydrogen atoms leading to isobutane formation[50d] is invalid. Tanner, et al. claimed the following:

1 - Only a small amount (0-16%) of the isobutane formed arises from benzylic hydrogen atom abstraction. Instead the major portion of tert butyl radicals undergoes cage and solution disproportionation to yield isobutane and isobutylene.[50d]

2 - There exists ambiguity in the mass spectroscopic analysis used by Pryor, et al. to obtain the relative rates of hydrogen atom abstraction from substituted toluenes by tert-butyl radical. For example, Tanner, et al. duplicated the rho value of 0.99[52a] at 30 °C when the ratio of isobutane to isobutane-2-d was determined using the method of Pryor. However, a rho value of 0.53 (r = 0.96) was obtained when the ratio is obtained from measurements of the contributions of $C_3C^{13}H_{10}$ (m/e 59.081605) and C_4H_9D (m/e 59.084527) ions to the (m/e 59) peak.

3 - Tanner, et al. also maintained that hydrogen atom abstraction from the sigma-complex intermediates that lead to formation of tert-butylated substrates (eq. 17) may compete with reaction under study (eq. 14).

The rho values obtained by Tanner are positive in agreement with Pryor's[50a,b] although their magnitudes are not as large as those previously reported.[50a,b] However, Tanner, et al. concluded that the positive rho values were solely due to viscosity effects on the cage disproportionation reaction of tert-butyl radical to isobutane and isobutylene.

In a subsequent paper Pryor, et al. reported their results on the investigation of hydrogen atom abstraction from a series of substituted toluenes by tert butyl

radical using an unambiguous method that does not require correction for viscosity effects.[50c] Pryor and coworkers used a competition technique between the chosen substituted toluene and toluene itself to obtain the relative rates for benzylic hydrogen atom abstraction by the tert-butyl radical.

Pryor and coworkers demonstrated that addition of tert-butyl radical to benzene is negligible, only 0.5% of tert-butyl benzene is formed at 80 °C. This modest addition of tert-butyl benzene to aromatic rings contrasts strongly with the well-known additions of methyl[58] and phenyl.[59] The results of a product study of the photodecomposition of AIB in toluene at different temperatures are compiled in Table 5. The data shows that 100 ± 2% of the theoretical yield of tert-butyl radical is recovered as isobutane (RH), isobutylene (R(-H)), 2,2,3,3-tetramethylbutane (RR), neopentylbenzene (QR), bibenzyl (QQ) and products represented (QR_2).

This product study does not substantiate Tanner's view.[50d] Tanner, et al. maintained that hydrogen atom abstraction from the cyclohexadienyl intermediate leading to tert-butylated substrates (eq. 17) could be a major source of isobutane formation. Pryor and coworkers reported that tert-butyltoluene was not detected. Furthermore, Tanner also argued that only (0-16%) of the isobutane formed arises from benzylic hydrogen atom abstraction. Pryor's results Table 5 are in disagreement with that view.

Pryor and coworkers used a complex kinetic analysis that took into account all the possible products to obtain the relative rates for hydrogen atom abstraction from substituted toluenes by tert butyl radical at 80 °C.[50c] Correlation against sigma substituent constants gave a rho value of 0.49 ± 0.04 at 80 °C. This value is in good agreement with the rho value of 0.59 reported by Fisher, et al. for their study on hydrogen atom abstraction from a series of substituted toluene by tert-butyl radical at 48 °C using an ESR technique to obtain the relative reactivities.

Table 5. Products[a] from the Photolysis of AIB[b] in Toluene.[c]

Products	40 °C	60 °C	80 °C	100 °C
Isobutane (RH)	98	111	117	125
Isobutylene (R(-H))	65	52	42	38
2,2,3,3-Tetramethylbutane (RR)	11	10	10	10
Neopentylbenzene (QR)	11	13	13	11
2,2,4-Trimethylpentane (RRH)	0.4	0.5	0.6	0.5
Isooctene (RR(-H))	1	1	1	1
2,2,4,4-Tetramethyl-1-phenylpentane (QR_2)	0.8	0.7	0.5	0.4
Bibenzyl (QQ)	11	20	30	39
Recovery of R group %	100	101	98	99
Q• formed %				
from RH (solution yield[d]	17	30	38	44
from Q-containing	17	27	37	45

[a] mol/100 mol of AIB decomposed
[b] $[AIB]_0$ = 0.0203 M
[c] $[Toluene]_0$ = 9.32 M
[d] 0.5 [RH-R(-H)]

Another well studied carbon-centered radical is undecyl (Un•). Henderson and Ward reported the results of the first Hammett study on hydrogen atom abstraction from a series of substituted toluenes by this radical.[52a] The undecyl radical was generated by thermolysis at 80 °C of lauroyl peroxide (LP) in a mixture of the substituted toluene (QH) and carbon tetrachloride. Carbon tetrachloride has been widely used as a reference in determining the relative reactivities of systems toward a variety of radicals.[14,35,60,61] The equations for the reaction of toluene with undecyl radical are summarized in Scheme 4.

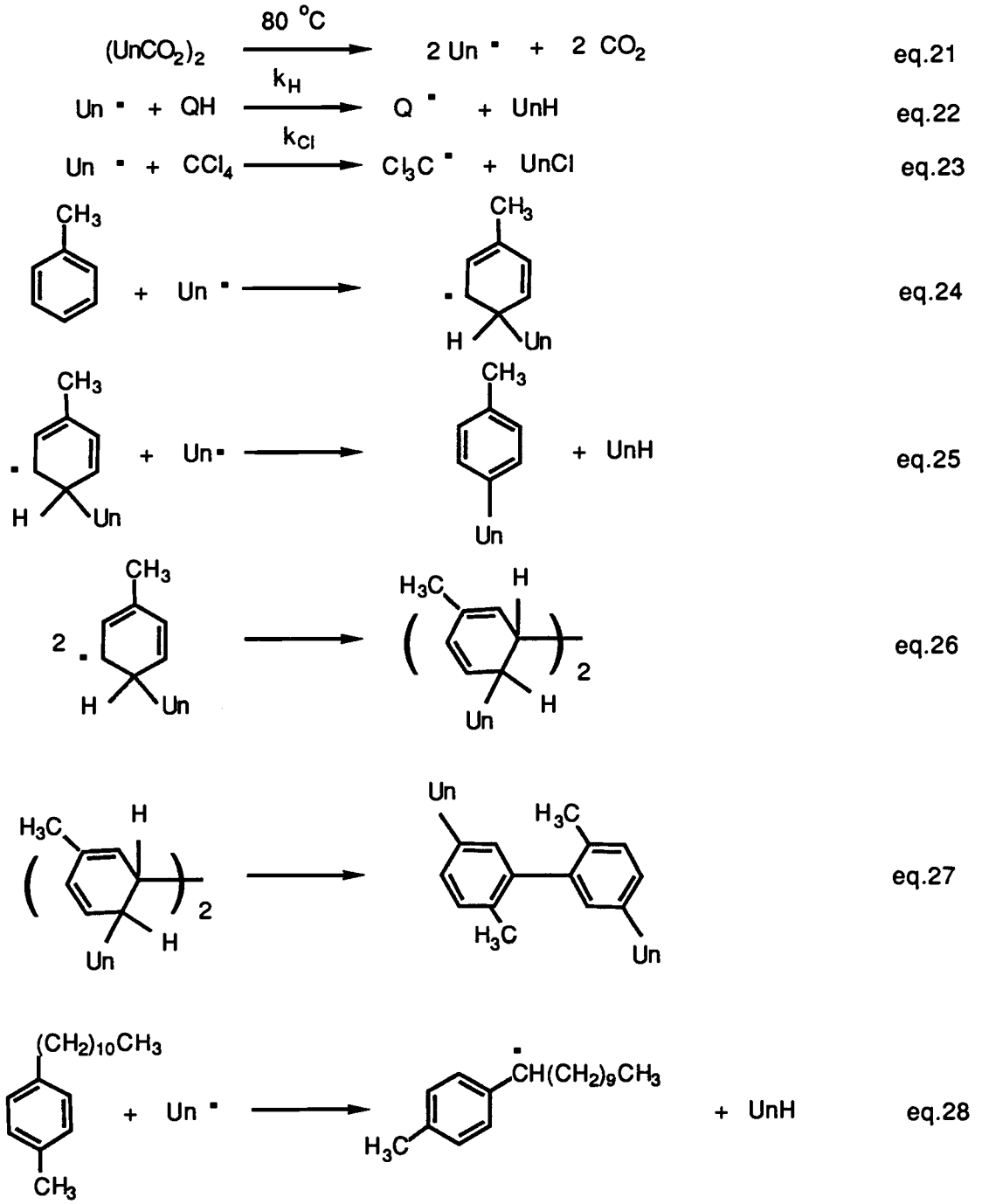
The relative reactivities of the substituted toluenes can be determined by measuring the amounts of undecane (UnH) to 1-chloroundecane (UnCl) formed. The reaction of UnH to UnCl is related to k_H/k_{Cl} by the equation shown below.

$$k_H/k_{Cl} = \frac{[UnH] - [UnH]_0}{[UnCl]} \cdot \frac{[CCl_4]}{[QH]} \qquad \text{eq. 29}$$

Some undecane was observed by Henderson and Ward even when the peroxide was decomposed in neat carbon tetrachloride. The concentration of undecane [UnH] produced should be corrected for this extraneous undecane $[UnH]_0$. The actual amount of this extraneous material was not reported.

The sole assumption made by Henderson and Ward in their kinetic analysis is that, in the presence of a hydrogen donor, the only sources for UnH and UnCl are those shown in equations 22 and 23, respectively. Henderson and Ward showed that other potential sources for undecane such as hydrogen atom abstraction from chloroform or the sigma complex intermediate of addition of undecyl radical to the aromatic ring (eq. 25) and hydrogen atom abstraction from secondary products such as undecylated substrates (eq. 28) are all negligible. The contribution of chloroform to UnH

Scheme 4


80 °C
(UnCO2)2
2 Un ▪ + 2 CO2
eq.21
kH
Un ▪ + QH
Q ▪ + UnH
eq.22
kCl
Un ▪ + CCl4
Cl3C ▪ + UnCl
eq.23
CH3
+ Un ▪
H
Un
eq.24
+ Un▪
+ UnH
eq.25
2
H3C
eq.26
eq.27
(CH2)10CH3
CH(CH2)9CH3
+ UnH
eq.28

production in the kinetic runs, although much greater than that of secondary products (eq. 25 - 28), is no greater than 2%.[52a] The other source of extraneous undecane is the reaction of undecyl radical with lauroyl peroxide. However, this process has been shown to be negligible at the concentration of lauroyl peroxide utilized to obtain the relative reactivities.[61b,63]

The relative rates for hydrogen atom abstraction from the a series of substituted toluenes by undecyl radical were obtained from the slope of the plot of [UnH] - $[UnH]_0$ vs $[CCl_4]/[QH]$. A Hammett sigma-rho plot gave a rho value of 0.45 ± 0.07 (r = 0.92) at 80 °C.[52a] The positive rho value has been ascribed to the contribution of the resonance structure IV to the hybrid description of the transition state.[50,51,52]

$$\underset{\text{I}}{[R{-}H\ {}^{\bullet}X} \longleftrightarrow \underset{\text{II}}{R^{\bullet}\ H{-}X} \longleftrightarrow \underset{\text{III}}{R^{+}\ H^{\bullet}\ {:}X^{-}} \longleftrightarrow \underset{\text{IV}}{R{:}^{-}\ H^{\bullet}\ X^{+}]}$$

Pryor and Davis reported[52b] their results on hydrogen atom transfer from substituted toluenes to undecyl radical at the same time as Henderson and Ward's findings were published.[52a] Pryor and Davis used a different analytical technique. Their kinetic system involves heating lauroyl peroxide at 81 °C in tert-butylbenzene solvent containing two substituted toluenes. The relative rates of hydrogen atom abstraction from the substituted toluene by undecyl radical are equal to the ratio of logarithms of the fractional amounts of the two toluenes remaining as measured by nmr.[64]

Pryor and Davis have shown that all secondary reactions that could lead to undecane formation are negligible if occurring at all.[52b] Correlation of the relative rates with sigma substituent constants gave an excellent correlation (r = 0.97) and a

rho value of 0.50 ± 0.02 at 81 °C.[52b] This value is in excellent agreement with the rho value 0.45 ± 0.07 (r = 0.92) reported by Henderson and Ward.[52a]

Zavitsas and Hanna[52c] have also reported their relative reactivities of a series of substituted toluenes toward undecyl radical in benzene solvent by measuring the disappearance of the chosen substituted toluene and toluene by gas-liquid chromatography.[49]

These authors' analysis indicates that the amount of undecane formed in the course of the reaction exceeded the combined amounts of the two toluenes reacted in all cases by about 25%. They attributed this to ring addition of undecyl radical.[52c] That conclusion was based on the following analogy. Methane-d is one of the products of the reaction of methyl radical with ring deuterated toluene.[62c]

These authors also pointed out the discrepancy between the value of relative reactivity for p-methoxytoluene determined by them (1.24 by GLG) and that of Pryor and Davis (0.69 nmr on benzylic CH_3).[52b]

If the data for p-methoxytoluene is disregarded, the Hammett plot for the remaining toluenes gives a rho value of 0.4.[52c] This is near the values reported by Henderson[52a] and Pryor.[52b] These two groups have described their Hammett correlation as reflecting exclusively benzylic hydrogen atom abstraction by undecyl radical,[52a,b] while Zavitsas and Hanna maintained that their data do not support such a rho value. This controversy emphasizes the need of obtaining fairly complete material balances in these studies.[65]

Atom abstraction is one of the most common free-radical reactions, with hydrogen[45,66] and halogen[67] being the most frequently transferred species. Halogen atom abstraction by Group IVB centered radicals is still under intense investigation. The special attention given to this process is spurred by its growing synthetic utility,[68] and its suitability for mechanistic studies. This process is illustrated in

equation 30 using the reduction of alkyl halides by Group IVB triorgano metal hydrides.

$$RX + R'_3MH \longrightarrow RH + R'_3MX \qquad \text{eq. 30}$$

$$M = Si, Ge, Sn, Pb$$

Even though organosilanes and organogermanes have also been investigated, triorganostannanes are the most widely studied. We will limit our discussion to the reaction of organic halides with organotin hydrides.

Carlson and Ingold, in their kinetic study of the reduction of a wide variety of halides by organotin hydrides, concluded that the reaction was highly selective.[69] Kuivila was the first to suggest a free radical mechanism for the reaction shown in equation 30.[70] Kuivila and others in subsequent publications showed convincingly that a free-radical chain mechanism was operative in the aforementioned reduction.[68,71] The rate determining step is a direct halogen atom abstraction by the triorganotin radical as shown in Scheme 5.

Scheme 5

$$\text{Initiator} \longrightarrow In^{\bullet} \qquad \text{eq. 31}$$

$$R'_3SnH + In^{\bullet} \longrightarrow R'_3Sn^{\bullet} + InH \qquad \text{eq. 32}$$

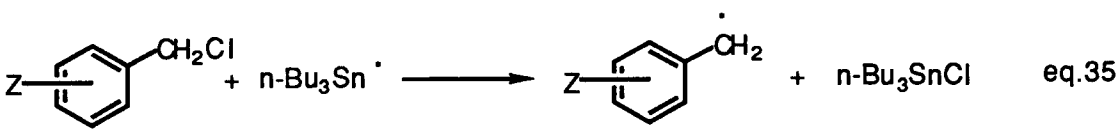
$$R'_3Sn^{\bullet} + RX \xrightarrow{\text{rds}} R'_3SnX + R^{\bullet} \qquad \text{eq. 33}$$

$$R'_3SnH + R^{\bullet} \longrightarrow R'_3Sn^{\bullet} + RH \qquad \text{eq. 34}$$

Kuivila and coworkers[68a,70,71a] and others[72] have reported that the reactivity of alkylhalides toward a given organotin hydride increases in the order RF < RCl < RBr < RI. For any given halogen the reactivity increases in the order primary < secondary < tertiary halide. Kuivila[71c] has reported that propargyl bromide was more reactive than allyl bromide toward tri-n-butyltin hydride. His explanation of this observation is that trialkyltin radicals are more nucleophilic relative to simple carbon radicals. Thus, polar factors may play a significant role in stabilizing the transition state by way of contributing structure shown below.

$$HC{\equiv}C{-}\overset{\delta-}{C}H_2 \cdots \overset{\bullet}{B}r \cdots \overset{\delta+}{Sn}R_3$$

Despite the uncertainty regarding the transition state of hydrogen atom abstraction, charge separation in the transition state of halogen atom abstraction by electropositive species is believed to play an important role.[71c] The view that studies utilizing triorganotin radical as abstracting agents could yield some insight into the role played by polar effect was put forward by Kuivila in 1964.[71a] However, it was Grady and coworkers who reported a positive rho value of 0.81 (r = 0.98) for chlorine atom abstraction from substituted benzylchlorides by tri-n-butyltin radical as shown below.[73]



eq.35

The Hammett plot for the data is presented in Figure 2. The positive rho value is consistent with the idea put forward by Kuivila[71c] that triorganotin radicals are

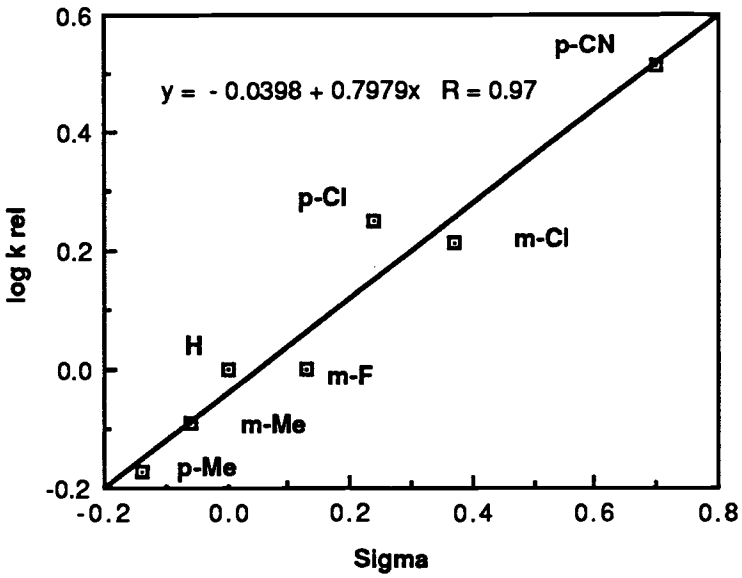


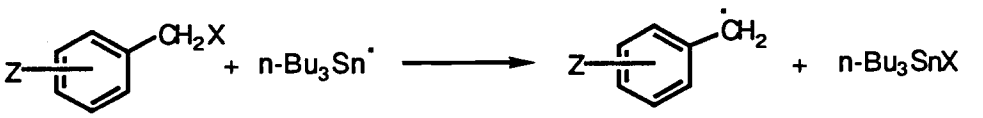
Figure 2. Hammett plot for reduction of benzyl chlorides by tri-n-butyltin hydride.

nucleophilic in nature. It is also consistent with the formalism that the transition state of chlorine atom transfer may be described as combination of the canonical forms shown in Figure 3, with a major contribution from canonical form IV.

$$\underset{\text{I}}{R\text{–}Cl\ {}^{\bullet}SnR'_3} \longleftrightarrow \underset{\text{II}}{R^{\bullet}\ Cl\text{–}SnR'_3} \longleftrightarrow \underset{\text{III}}{R^{+}\ \overset{\bullet}{Cl}\ \overset{\bullet\bullet^{-}}{SnR_3}} \longleftrightarrow \underset{\text{IV}}{R^{\bullet\bullet}\ \overset{-\ \bullet}{Cl}\ {}^{+}SnR'_3}$$

Figure 3. Structure of the transition state for the reaction of alkyl chloride with trialkyltin radical.

Tanner and Blackburn reexamined and extended the original work to include the benzyl bromides and benzyl iodides as shown in equation 36.[74] They observed no reduction of the corresponding benzyl flourides under their reaction conditions.



eq.36

X = Cl, Br, I

However, the transfer of iodine atom to the tri-n-butyltin radical shows an anomalously high rho value compared to that of the corresponding chlorides or bromides as shown in Table 6.

Table 6. Rho Values for the Reaction of α-Halotoluenes with Tri-n-butylstannane in Benzene at 90°C.[74]

	σ^-		σ	
α–Halotoluene	ρ	r[b]	ρ	r[b]
α-Chloro[a]	0.33	0.96	0.42	0.97
α-Chloro	0.34	0.97	0.40	0.92
α-Bromo	0.17	0.98	0.22	0.95
α-Iodo	0.81	0.99	1.05	0.94

[a] Ref. 73

[b] Correlation coefficient

They also observed an increased sensitivity to solvent polarity for iodine atom transfer relative to bromine and chlorine atom transfers. These observations led Tanner and Blackburn to propose two alternative mechanisms for iodine atom abstraction by tri-n-butyl stannane. These two mechanisms are presented below. The first is analogous to that suggested by Sukarai for the reduction with triethyl-

germane.[76] It involves the formation of an intermediate with an expended octet at the halogen atom (eq. 38).

Scheme 6

$$R_3SnH + In^{\bullet} \text{ (initiator)} \longrightarrow R_3Sn^{\bullet} + InH \qquad \text{eq. 37}$$

$$Ar\text{–}CH_2\text{–}X + R_3Sn^{\bullet} \rightleftharpoons [ArCH_2\text{–}\overset{\delta-}{X}\cdots\overset{\delta+}{Sn}R_3]^{\bullet\ddagger} \rightleftharpoons ArCH_2\text{–}\overset{\bullet}{X}\text{–}SnR_3 \qquad \text{eq. 38}$$

$$ArCH_2\text{–}\overset{\bullet}{X}\text{–}SnR_3 \longrightarrow [ArCH_2\cdots\overset{\delta-}{X}\text{–}\overset{\delta+}{Sn}R_3]^{\bullet\ddagger} \longrightarrow Ar\overset{\bullet}{C}H_2 + XSnR_3 \qquad \text{eq. 39}$$

However, the report that the reactivity of alkyl halides[71b] is RI > RBr > RCl > RF and the fact that the reduction of aralkyl fluorides in solution has been reported[71b,68a] as well as the gas-phase reduction of primary and secondary alkyl fluorides[71d] caused Tanner and Blackburn to conclude that this alternative mechanism is not correct. This mechanism would necessitate that a first-row element (fluorine) expends its octet, a process which is not allowed. The second free-radical chain mechanism proposed by Tanner and Blackburn[74] involves an electron transfer reaction in its propagation sequence as depicted in equation 41.

Scheme 7

$$R_3SnH + In^{\bullet} \longrightarrow R_3Sn^{\bullet} + InH \qquad \text{eq. 40}$$

$$ArCH_2X + R'_3Sn^{\bullet} \longrightarrow ArCH_2X^{\bullet -} + R_3Sn^{+} \qquad \text{eq. 41}$$

$$ArCH_2X^{\bullet -} \longrightarrow ArC^{\bullet}H_2 + X:^{-} \qquad \text{eq. 42}$$

Electron transfer processes, such as that depicted in eq. 41, should show a positive Hammett rho value with an expected correlation with sigma-minus substituent constants. The polarographic half-wave potentials for the reduction of benzyl bromides,[77] and benzyl chlorides[78] showed this behavior. Tanner and Blackburn concluded that, at least for iodine atom abstraction, the electron-transfer mechanism is operative. However, they failed to indicate into which orbital of the benzyl iodide the electron is transferred. In a later paper Gleicher, et al. reported the results of the study of iodine atom abstraction from polycyclic iodomethylarenes by the nucleophilic triphenyltin radical.[79] Their results support Tanner's view that an electron is transferred in the propagation sequence. Gleicher, et al. also suggested that the electron is transferred to the low laying σ^* orbital of the exocyclic carbon-iodine bond.

In a complementary experiment Kochi used the kinetic isotope effect to ascertain the extent of bond breaking and electron transfer in the reaction of methyl halides with triphenylstannane. The results of this study are shown in Table 7.

Table 7. Carbon-13 Kinetic Isotope Effect for Halogen Atom Transfer from Methyl Halides to Triphenyltin Radical.

Methyl halide	k_{12}/k_{13}	Initiation Mode
Methyl iodide	1.0136 ± 0.0010	Thermal
Methyl iodide	1.0126 ± 0.0002	Photolytic
Methyl bromide	1.0350 ± 0.0013	Photolytic
Methyl chloride	1.0475 ± 0.0014	Photolytic

Values of the kinetic isotope effect larger than the equilibrium isotope effect (which have been calculated to be 1.027 for CH_3I and 1.035 for CH_3Cl)[81] reflect the extensive bond breaking, generally meaning a late transition state.[82] Thus, Kochi concluded that while chlorine and bromine atom abstraction proceeds with substantial bond breaking in the transition state, there is little bond breaking for iodine atom abstraction. Kochi also pointed out that the marked change in the slope of the curve in Figure 4 is suggestive of a different type of interactions in the iodine atom transfer from those of chlorine and bromine. Kochi's observations clearly support Tanner's proposal of a mechanism for iodine atom abstraction by triorganotin radicals different from that of chlorine and bromine atom abstraction.

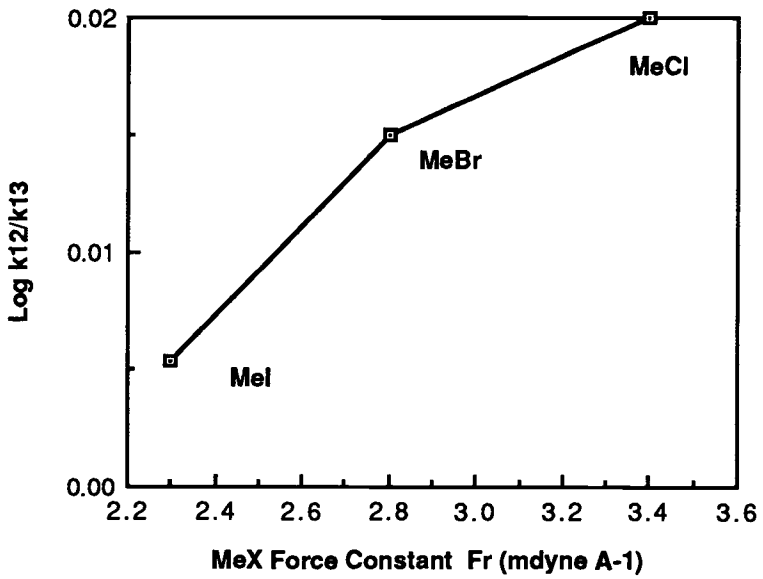


Figure 4. Variation of the kinetic isotope effect for halogen atom transfer from methyl halides to triphenyltin with the carbon-halogen stretching force constant Fr.

DISCUSSION OF THE PROBLEM

One of the many utilizations of molecular orbital theory has been in the investigation of arylmethyl intermediates (eq. 43) and the correlation of their rates of formation with calculated energy difference between said intermediate and the parent arene.[83]

$$ArCH_2X \longrightarrow ArCH_2 \left(\begin{smallmatrix} + \\ - \end{smallmatrix} \right) + X \left(\begin{smallmatrix} - \\ + \end{smallmatrix} \right) \qquad \text{eq.43}$$

Several studies involving correlation of rates of arylmethyl carbocation formation have been repoted. Dewar and Sampson studied the solvolysis of arylmethyl chlorides in aqueous formic acid.[84] The reaction is believed to proceed with an S_N1 mechanism. Dewar and Sampson also studied the reaction when a less ionizing solvent (80% aqueous alcohol) is employed. Here the S_N2 mechanism is though to be the major pathway.[85] Fierens' group has also investigated the same systems in a ternary solvent of water, dioxane and formic acid.[86] Berliner and Shieh extended this type of analysis to the solvolysis of 1-arylethyl chlorides in 80% aqueous acetone.[87]

The formation of arylmethyl carbanions has been studied as well. Streitwieser and Langworthy examined the rates of lithium cyclohexylamide catalyzed hydrogen-deuterium exchange of a variety of deuteriomethylarenes in cyclohexylamine.[88] This reaction is well known to involve a carbanion intermediate.[89]

It is rather surpising that, unlike the arylmethyl ions, a systematic experimental investigation of the formation of the corresponding arylmethyl radical had not received earlier attention. Until two decades ago, the only report on correlation of the rates of formation of arylmethyl radicals with molecular orbital calculated quantities was the work of Kooyman.[90] Kooyman attempted the investigation of hydrogen atom

abstraction by trichloromethyl radical from a series of aralkyl compounds and olefins.[90] A low correlation coefficient (0.47) was obtained when Kooyman correlated the logarithms of the relative rates with HMO pi energy differences. This may be attributed both to the structural dissimilarity of the compounds involved and the predominance of radical addition in specific systems. The application of molecular orbital theory to studies involving formation and reactivity of free radicals has increased in the recent years.[91] Gleicher and Unruh investigated hydrogen atom abstraction from homoarylmethanes by radicals generated from bromotrichloromethane.[92] The relative reactivities were evaluated by direct competitive studies involving diappearance of starting material. Trichloromethylation of the rings was corrected for by competitive investigation involving the parent arenes. Possible errors due to substituent effects of the methyl group were shown to be small.[93] The reaction is shown in eq. 44.

$$ArCH_3 + BrCCl_3 \xrightarrow[\text{peroxide}]{70\ ^\circ C} ArCH_2Br + HCCl_3 \qquad \text{eq.44}$$

A good correlation (r = 0.98) was obtained when the logarithms of the relative rates were plotted against SCF calculated energy differences. The plot is shown in Figure 5. Gilliom's group obtained similar results when they investigated the same systems using bromine atom as the abstracting agent.[94] Gleicher and Church investigated benzylic radical formation by the addition of thiyl radical to alkenylarenes.[95] The reaction is shown below.

$$Ar\overset{\overset{Z}{|}}{C}{=}CH_2 + PhS^{\bullet} \xrightarrow{70\ ^\circ C} Ar\underset{\underset{\bullet}{|}}{\overset{\overset{Z}{|}}{C}}{-}CH_2SPh \qquad \text{eq.45}$$

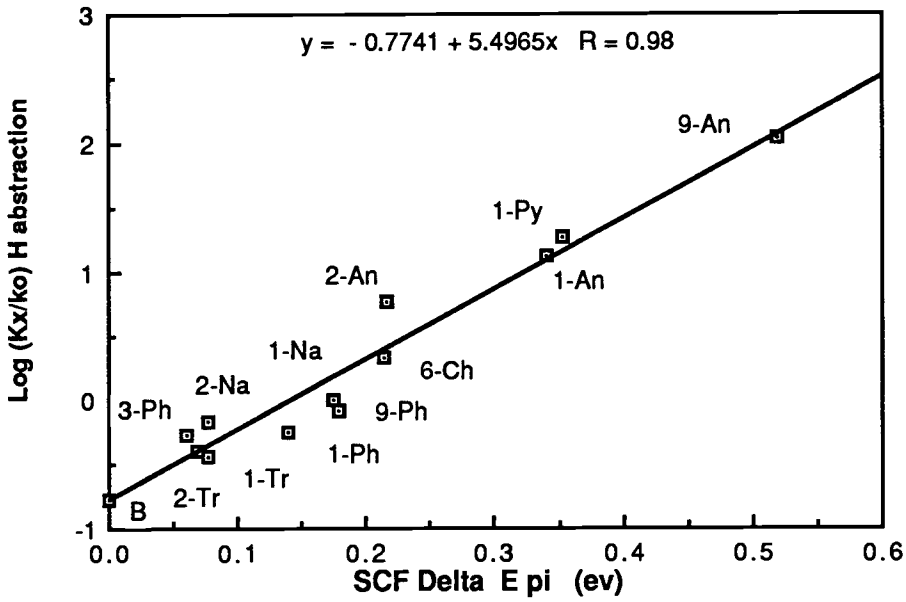


Figure 5. Correlation of relative rates of hydrogen atom abstraction from a series of homoarylmethantes by trichloromethyl radical with relative (benzene-benzyl) SCF pi energy differences.

For Z = H, they obtained a relatively good correlation (r = 0.92) when the logarithms of the relative rates were plotted against SCF calculated energy difference (figure 6).

It should be pointed out, however, that even though these polycyclic substrates are very amenable to molecular orbital correlation,[91] they do not provide any insight into the point raised by Zavitsas and Pinto.[49] Because of their alternant nature, the benzenoid systems utilized in thses studies[91,93,94] led to parallel trends of calculated energies for the carbocation, the carbanion and the radical intermediates.[98] For alternant hydrocarbons there are well defined electronic relationships among the pi electrons. In particular, there is a uniform charge density at each conjugated atom. This allows for separation of resonance and inductive effects. Thus,

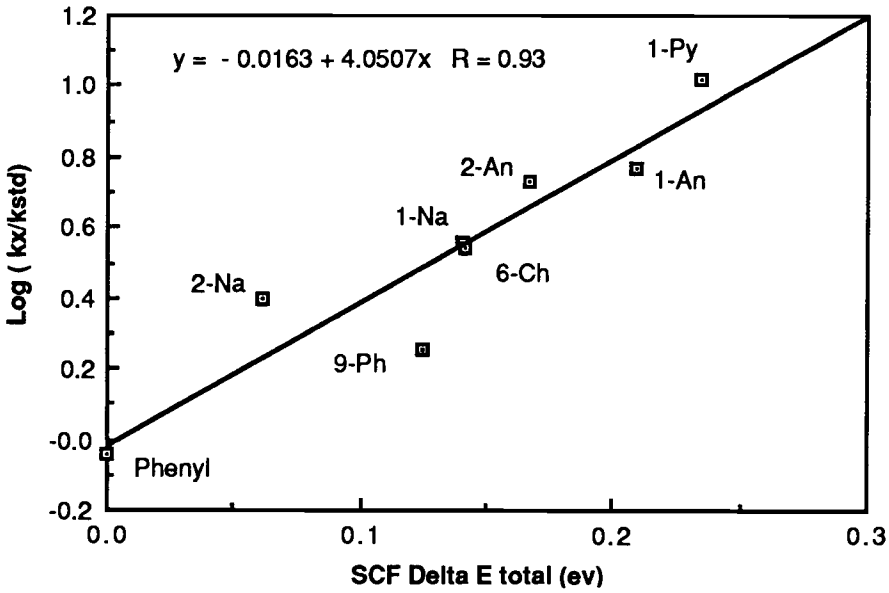
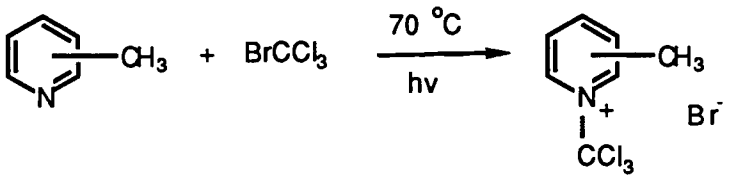


Figure 6. Correlation of relative rates of addition of thiophenol to vinylarenes with SCF total energy differences.

any change in reactivity can be traced solely to resonance stabilization of the radical intermediate since each aryl group will exert a common inductive effect in a radical generating reaction.[97] Insight into the question of charge separation may be obtained, however, by the inclusion of heteroaromatic systems in the studies. Replacement of one or more CH units with isoelectronic nitrogen, oxygen or any other heteroatom will destroy the uniform pi electron distribution and should change the overall inductive properties of the aryl group. Therefore, the concept of inductive equivalence among the homoaryl groups will no longer be valid.

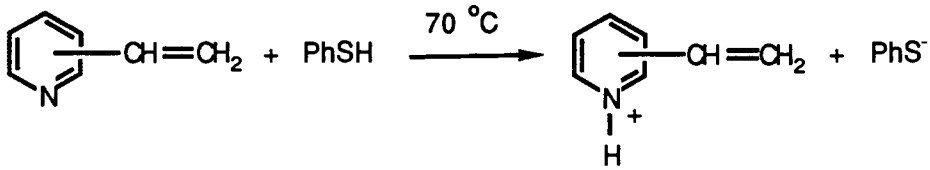
Gleicher and coworkers were among the first to test the above hypothesis. They originally hoped to extend the already presented hydrogen atom abstraction[92] and the thiyl radical addition[95] to studies involving heteroaromatic systems. These early attempts proved to be unsatisfactory.[98] Hydrogen atom abstraction from

isomeric picolines by trichloromethyl radicals was not observed. The electrophilic trichloromethyl radical prefers to react at ring nitrogen rather than abstract a benzylic hydrogen. This is shown in equation 46.



eq.46

The corresponding addition of thiyl radical to vinylpyridines also led to reaction at the ring nitrogen as shown in equation 47.



eq.47

Because of the prevalence of these "side reactions", competitive studies involving disappearance of starting materials cannot be employed.

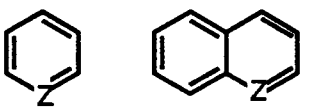
Gleicher and Mahiou, however, were able to utilize molecular orbital correlations to provide some insight into the controversional question of possible charge separation developed in the transition state of hydrogen atom abstraction.[99] The authors investigated hydrogen atom abstraction from a series of homoaryl and heteroarylmethanes by the electrophilic tert-butoxyl radical at 70 °C (eq. 48).

This system was chosen for several reasons.

a - The reaction of tert-butoxyl radical with the heteroaromatic should not lead to quaternization of the ring nitrogen.

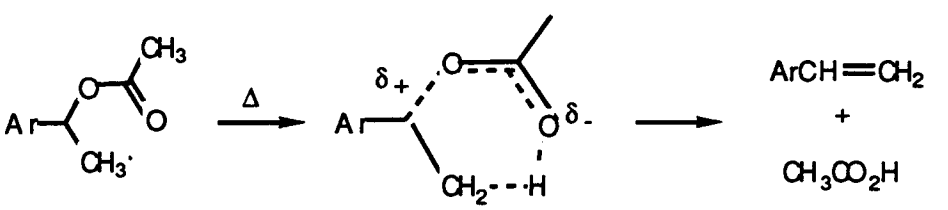
$$ArCH_3 + (CH_3)_3CO^{\bullet} \xrightarrow{70\,^{\circ}C} Ar\dot{C}H_2 + (CH_3)_3COH \qquad \text{eq.48}$$

$$(CH_3)_3CO^{\bullet} \longrightarrow CH_3COCH_3 + \dot{C}H_3 \qquad \text{eq.49}$$

Ar =  Z = CH, N

b - The major advantage this system offers is the presence of an internal "clock" reaction (eq. 49) which allows for an unambiguous determination of the relative rates by evaluation of the tert-butyl alcohol to acetone ratio. This is independent of extraneous reactions of the substrate molecules.[11,12]

Correlation of the results involved plotting the logarithms of relative rates of hydrogen atom abstraction against SCF calculated energy differences between transitions state and parent arenes. Transition states were assumed to structurally resemble carbocation, carbanion or radical intermediates. Optimum correlation (r = 0.92) was obtained when a carbocation transition state model was utilized (figure 7). An even better correlation (r = 0.97) was obtained when the logarithms of the realtive rates of hydrogen atom abstraction were plotted against those from the pyrolysis of the corresponding 1-homoaryl and 1-heteroarylethyl acetates[100-102] (eq. 50). The correlation plot is shown in figure 8.



eq. 50

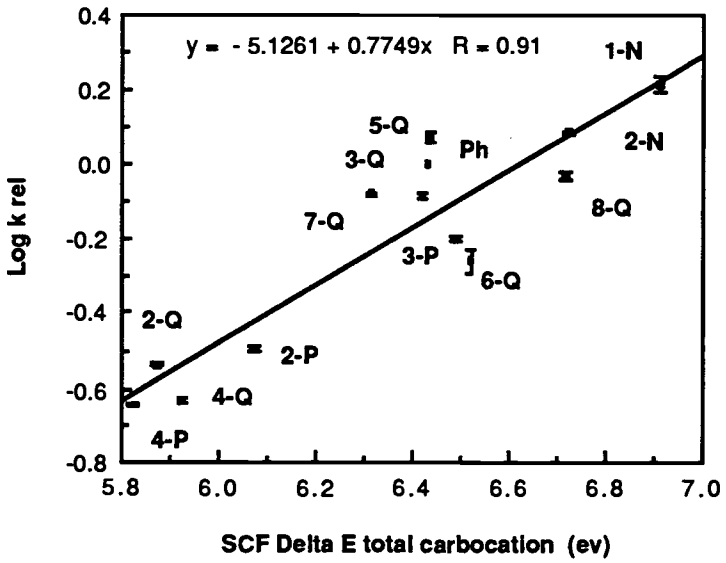


Figure 7. Correlation of relative rates of hydrogen atom abstraction by tert-butoxyl radical from a series of homoaryl and heteroarylmethanes with SCF total energy difference using a carbocation model.

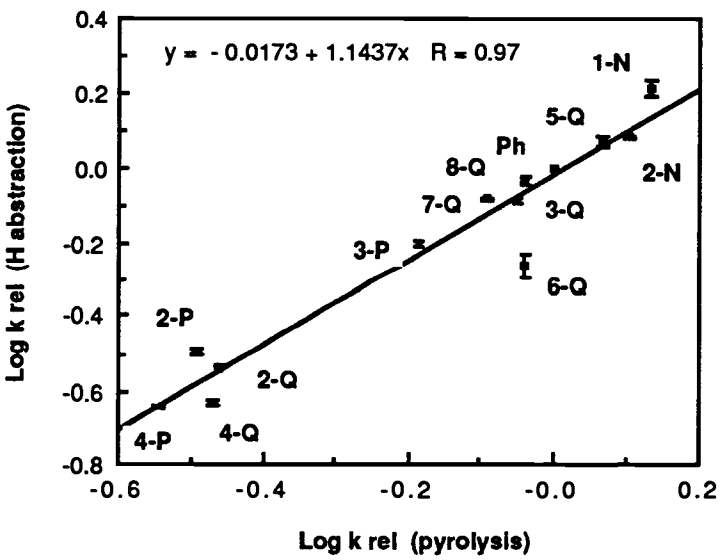
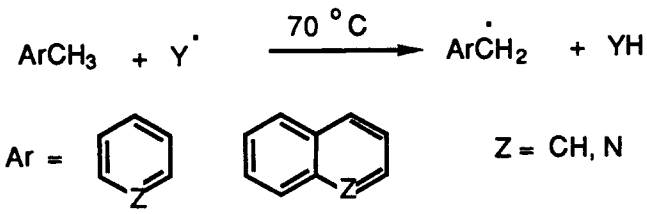


Figure 8. Logarithms of relative rates of hydrogen atom abstraction by tert-butoxyl radical from a series of homoaryl and heteroarylmethanes versus the values for the pyrolysis of the corresponding 1-arylethyl acetate.

The pyrolysis reaction is known to involve a transition state in which an appreciable positive charge is developed at the benzylic position. Gleicher and Mahiou concluded that their results tend to support the view that there is a substantial positive charge development in the transition state of benzylic hydrogen atom abstraction by the electrophilic tert-butoxyl radical.[99]

In view of the above results, it would be interesting to extend this type of analysis to the study of hydrogen atom abstraction from the same series of unsubstituted homoaryl and heteroarylmethanes by a nucleophilic radical (eq. 51). Application of molecular orbital calculations to model the transition might again provide some evidence on the question of charge separation in the transition state of the reaction.



eq.51

The radical chosen for this investigation is undecyl radical (Un•). This radical was derived from lauroyl peroxide (LP). Several reasons favored the choice of this species.

a - The undecyl radical is easily generated by thermal decomposition of lauroyl peroxide.[52]

b - Hydrogen atom abstraction from substituted toluenes has been well investigated.[52] The undecyl radical is known to be nucleophilic. Rho values in the range of +0.4 to +0.5 have been obtained.[52]

c - The reaction can be run in the presence of carbon tetrachloride. Carbon tetrachloride has been widely used to determine the relative reactivities

of systems toward a variety of radicals:[14,35,60,61] this is illustrated in scheme 4 and equations 22 and 23. Under these conditions, the rates of hydrogen atom abstraction from the chosen substrates by undecyl radical can be easily obtained from equation 52.

$$k_H/k_{Cl} = \frac{\text{undecane}}{\text{1-Chloroundecane}} \cdot \frac{[CCl_4]}{[QH]} \qquad \text{eq. 52}$$

By focusing attention on product formation, problems associated with disappearance of substrates by competing reactions are minimized.

The replacement of the CH unit by the isoelectronic nitrogen will again destroy the uniform pi electron distribution and change the inductive characteristics of the heteroaryl groups. This will allow us to evaluate possible charge development in the transition state.

Gleicher and Soppe-Mbang used the same approcah to investigate chlorine atom transfer from homoarylmethyl chlorides[103] and heteroarylmethyl chlorides[104] to the nucleophilic triphenyltin radical at 70 °C.

$$ArCH_2Cl + Ph_3Sn^{\bullet} \xrightarrow{70\ ^{\circ}C} Ar\dot{C}H_2 + Ph_3SnCl \qquad \text{eq.53}$$

These authors utilized oxygen containing heteroarylmethyl chlorides to evaluate possible charge development in the transition state of the reaction depicted in equation 53. They concluded that the rate determining step is a direct atom abstracton. Optimum correlation was obtained when a carbanion model was used for the transition state. The plot of the logarithms of the relative rates against SCF calculated energy difference between the intermediate carbanion and the parent arene is shown in figure

9. This led the authors to emphasize the importance of charge separation in the transition state of halogen atom abstraction by nucleophilic tin radicals.[104] These results also led Gleicher and Soppe-Mbang to conclude that canonical form IV (figure 3) is the major contributing atom transfer to the nucleophilic triphenyltin radical.[104]

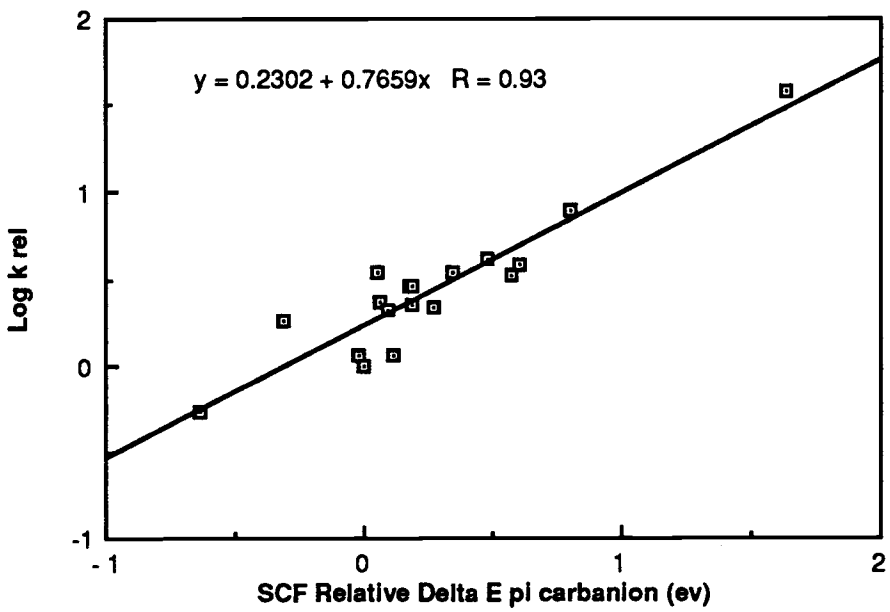
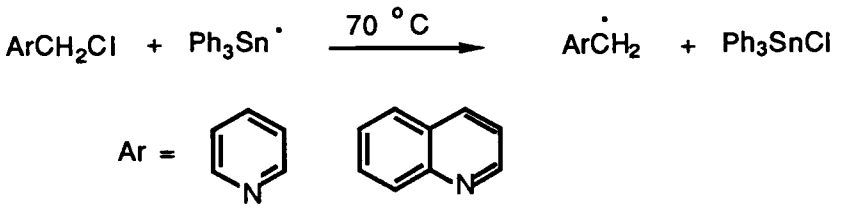


Figure 9. Logarithms of relative rates of chlorine atom abstraction by triphenyltin radical from homo and heteroarylmethyl chlorides versus SCF relative energy differences using a carbanion model.

It would be interesting to extend this type of analysis to investigate chlorine atom transfer from nitrogen containing heteroarylmethyl chlorides to the triphenytin radical (eq. 54).

It would also be interesting to see whether the application of molecular orbital theory could allow us to conclude whether the reaction involved direct atom transfer, similar to that proposed for the case of oxygen containing heteroarylmethyl



eq.54

chlorides,[105] or instead involved an electron transfer. The latter possibility has been observed for the reaction of tributyltin radical with substituted benzyl iodide[74] and triphenyltin radicals with polycyclic iodomethylhomoarenes.[79]

RESULTS AND DISCUSSION

I. Preparation of the Compounds.

Picolines and methylquinolines were purchased save for 5-methylquinoline which was prepared by a standard route.[99]

The heteroarylmethyl chlorides utilized in the study of chlorine atom transfer came from three sources:

A. Some of the compounds were commercially available such as 1-chloromethylnaphthalene and 2- and 4-chloromethylpyridine. However, the latter two were obtained as hydrochloride salts.

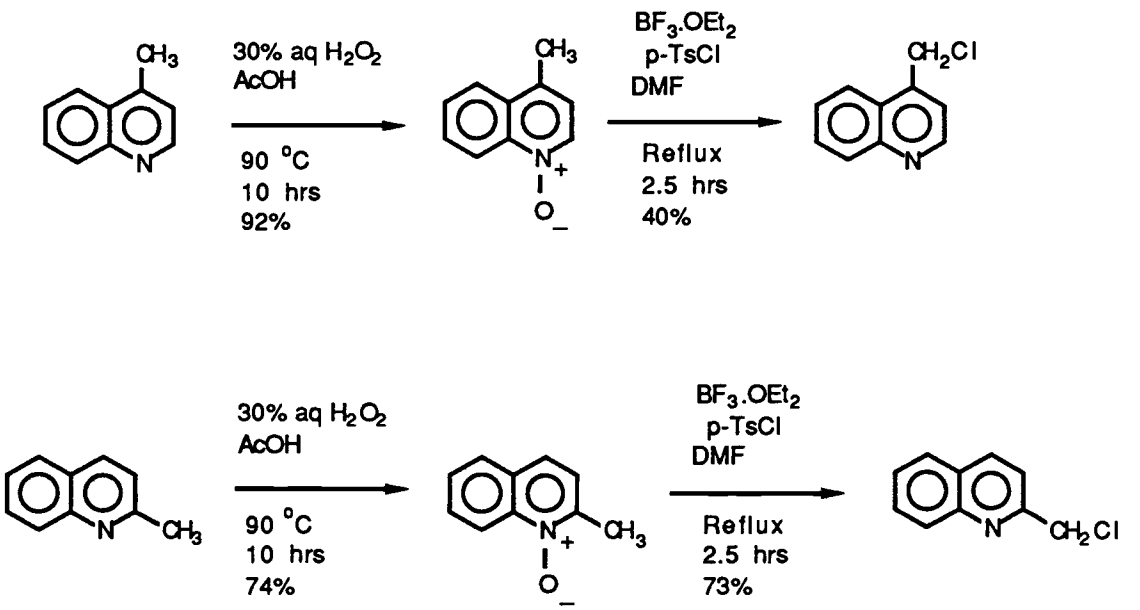
B. 3-Chloromethylpyridine was prepared from the corresponding carbinol.

C. The majority of the chloromethylquinoline isomers were prepared from the corresponding methylquinolines by either of the two methods described below. The only exception was the 3-isomer which was prepared by a different route starting with 3-bromoquinoline.

Preparation of chloromethylquinoline isomers.

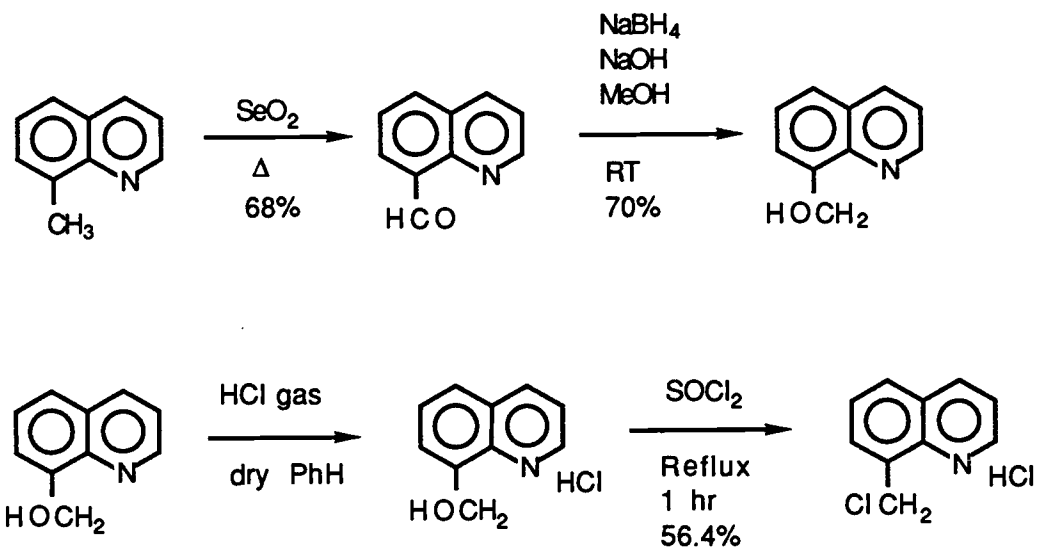
Method 1: The 2- and 4-chloromethylquinoline were prepared from the corresponding N-oxides[105] by the method of Ochiai.[106] The reactions are depicted in Scheme 8.

Scheme 8


CH3
30% aq H2O2
AcOH
90 °C
10 hrs
92%
N
N+
O_
BF3.OEt2
p-TsCl
DMF
Reflux
2.5 hrs
40%
CH2Cl
30% aq H2O2
AcOH
90 °C
10 hrs
74%
BF3.OEt2
p-TsCl
DMF
Reflux
2.5 hrs
73%

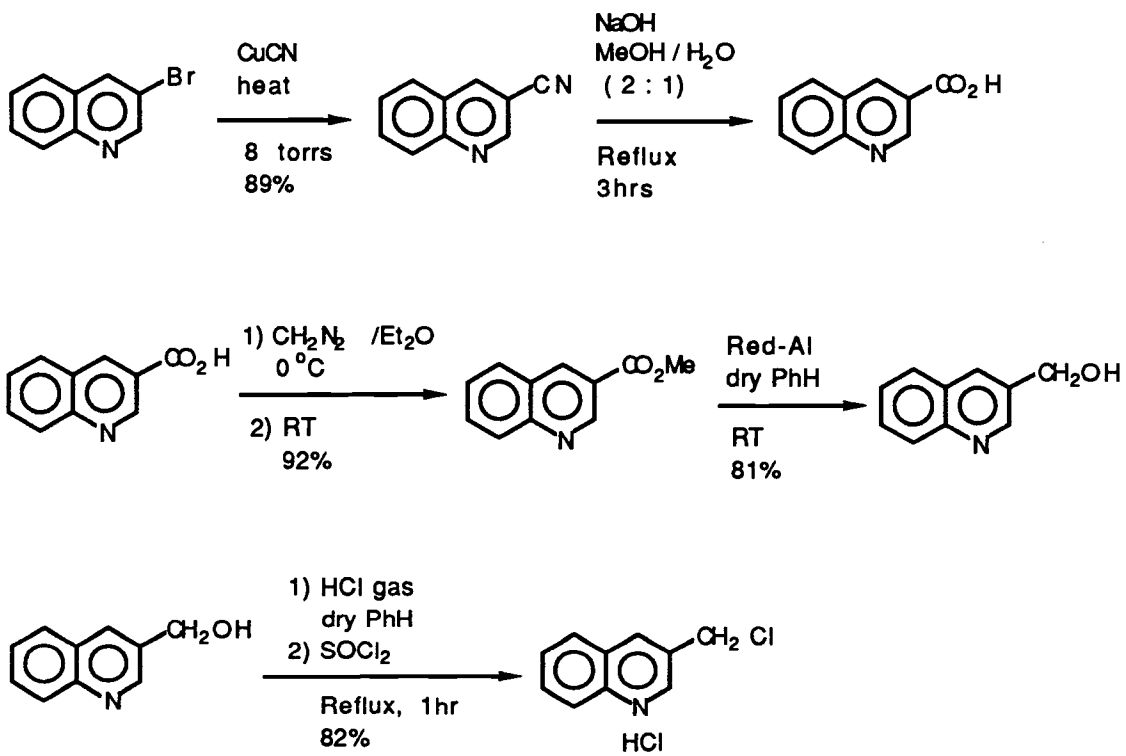
Method 2: The 5, 6, 7, and 8 isomers of chloromethylquinoline were prepared from the corresponding carbinols using Kaslow and Schlatter's procedure.[107] The carbinols were obtained by reduction of the quinoline carbaldehydes. The aldehydes were prepared by selenium oxide oxidation of the corresponding methylquinolines.[108] The synthetic route is shown in Scheme 9 using the preparation of 8-chloromethylquinoline as an example.

Scheme 9



3-Chloromethylquinoline was prepared from 3-hydroxymethylquinoline by the method of Kaslow.[107] The carbinol was obtained by the bis(2-methoxyethoxy)aluminum hydride reduction of methyl 3-quinolinecarboxylate. The ester was synthesized from 3-bromoquinoline in three steps. The preparation of 3-chloromethylquinoline is outlined in Scheme 10.

Scheme 10



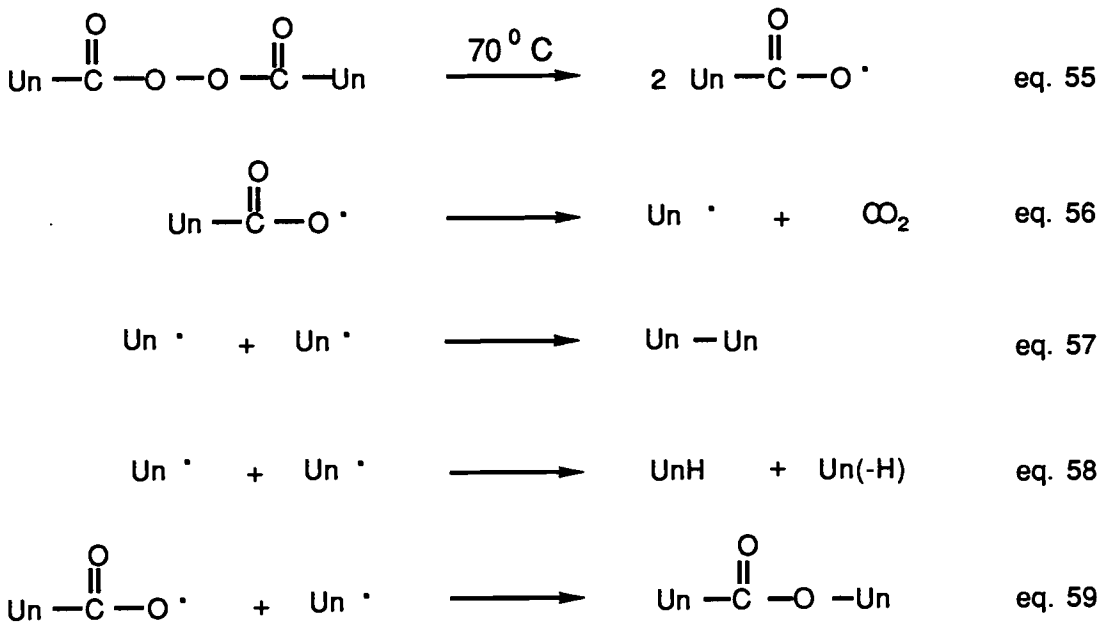
All the heteroarylmethyl chlorides investigated in this study are labile. They were prepared and purified just prior to their utilization. Their purity was checked by nuclear magnetic resonance. Only signals expected for the given compounds were observed. Details on the preparation of individual compounds are found in the experimental section.

II. Relative Rates of Hydrogen Atom Abstraction from a Series of Homoaryl and Heteroarylmethanes by Undecyl Radical.

The undecyl radical (Un•) was generated by the thermolysis of lauroyl peroxide (LP) at 70 °C in an equimolar solution of the chosen hydrogen donor (QH) and carbon tetrachloride. Due to the complexity of the overall system, the equations for possible reactions have been divided into several schemes on the basis of their general class. Scheme 11 shows initiation and cage reactions, Scheme 12 summarizes the primary (non cage) product forming reactions, Scheme 13 describes the secondary (non cage) product forming reactions and Scheme 14 depicts the possible fate of the incipient benzylic radical.

Scheme 11

Initiation and cage reaction



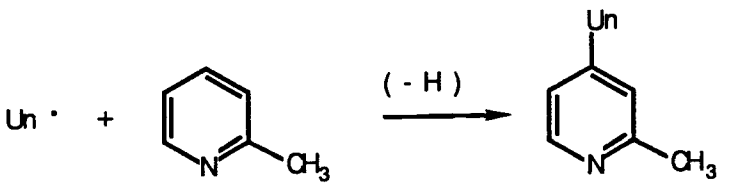
Un = n-$C_{11}H_{23}$

Scheme 12

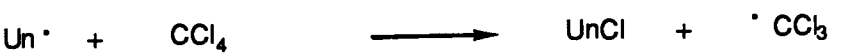
Primary (non cage) product forming reactions.

(2-methylpyridine is used as an example)

eq . 60



eq . 61



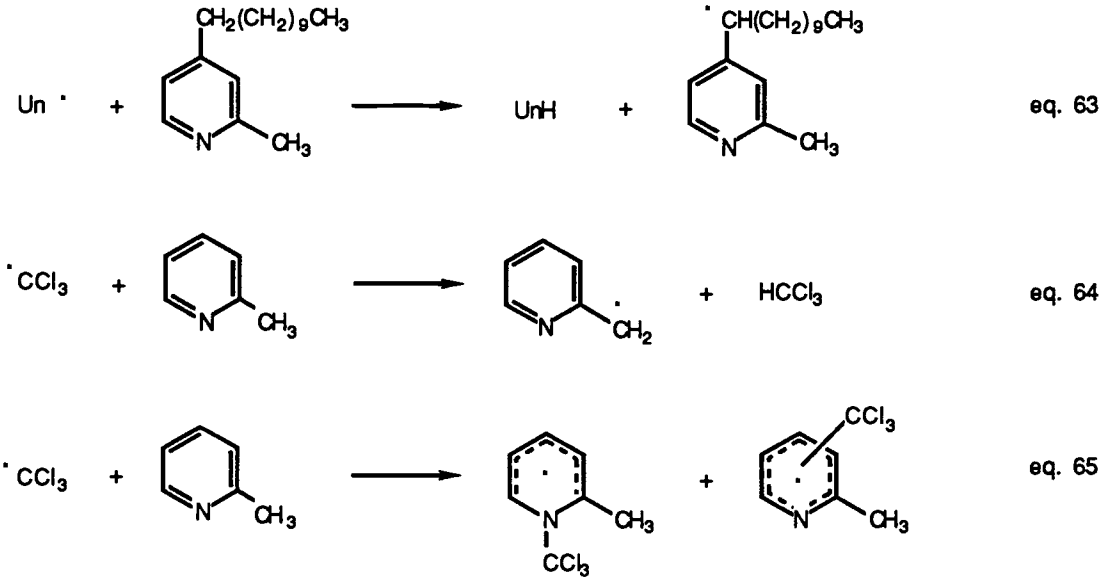
eq . 62

Un = n - $C_{11}H_{23}$

Scheme 13

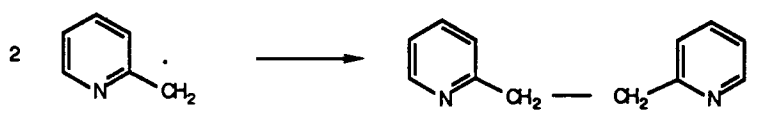
Secondary (non cage) product forming reactions.

(2-methylpyridine is used as an example)

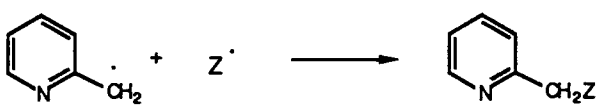


Scheme 14

Possible fate of the benzylic radical. (2-methylpyridine is used as an example)

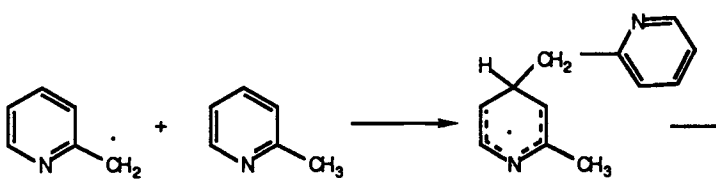


eq . 66



eq . 67

Z = Un , CCl_3 , R—C(=O)—O



Dimerization,
Disproportionation
or Rearomatization.

eq . 68

Solutions of lauroyl peroxide, carbon tetrachloride and the arylmethanes were prepared in the ratio 1:50:50. These solutions were equally divided into several ampoules. After a series of freeze-thaw cycles, the ampoules were sealed under a reduced pressure of nitrogen. They were then placed for 90 hours in a constant temperature oil bath maintained at 70 ± 1 °C. This time corresponds to several half lives of lauroyl peroxide. Examination of final reaction mixtures by i.r. spectroscopy showed no detectable LP to be present. The decomposition of the peroxide during GLC analysis of reaction mixtures could seriously modify the results. After completion of the reaction the ampoules were cooled and opened. Aliquots of the reaction mixture were diluted to 10 mL with a 9.521 x 10^{-4} M solution of the GLC internal standard chlorobenzene in acetone. This solution was then analyzed for undecane, 1-undecene and 1-chloroundecane.

Gas-liquid chromatographic analysis was carried out with either Varian 3300 or Varian 3400 capillary gas chromatograph equipped with an FID detector, 30m x 0.25mm DB-5 capillary column and a Varian 4290 integrator. Helium was the carrier gas and individual samples were analyzed in replicate.

The relative reactivities of the homoaryl and heteroarylmethanes can be determined by measuring the amounts of undecane (UnH) and 1-chloroundecane (UnCl) formed.[52a] The ratio of undecane to 1-chloroundecane is related to k_H/k_{Cl} by the equation shown below.

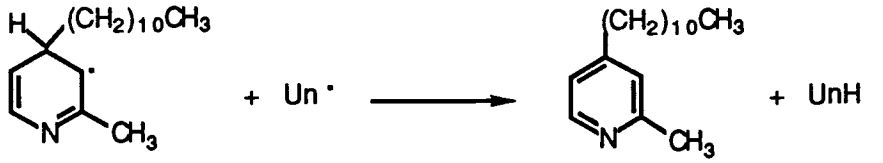
$$k_H/k_{Cl} = \frac{\text{Undecane}}{\text{1-Chloroundecane}} \cdot \frac{[CCl_4]}{[QH]} \qquad \text{eq. 52}$$

Before the amount of undecane can be equated with the rate of hydrogen atom abstraction, it is necessary to make sure that all the undecane arises from hydrogen

atom abstraction from the exocyclic methyl group of the initial substrates and not from any other reaction. Because of possible side reactions which can lead to the formation of undecane by hydrogen atom abstraction from secondary products solutions of lauroyl peroxide and donor in a low ratio (1:50) were utilized. Under such conditions, the possibility of induced decomposition of the starting peroxide should be minimal.[109] This would also ensure that other sources of abstractable hydrogen atoms such as undecylated substrates formed via (eq. 61), 1,2-diarylmethanes formed by dimerization of the benzylic radical (eq. 66) and diaryl methane arising from the benzylation of substrate (eq. 68) would be present in very small amounts. The abundance of undecylated secondary products and dimer relative to starting substrate are 4 and 2%, respectively. These secondary products would show variable hydrogen atom donor abilities. Diarylmethanes should be particularly prone to undergo hydrogen atom abstraction. However, the amount of diarylmethane, if present, should be very small. Benzylic radicals are known to undergo dimerization more readily than addition to the aromatic portion of the substrate.[32,36,110] Johnston and Williams,[32,36] in the study of hydrogen atom abstraction from picolines and substituted toluenes by the tert-butoxyl radical, reported that the major products obtained were coupling products (dimers) with no detectable diarylmethanes being observed. Even though these secondary benzylic systems are potential sources for hydrogen atom abstraction, the maximum concentration mentioned above is never reached. Other products predominate even in the case of the least reactive substrate investigated in this study. The presence of these secondary benzylic systems should affect the ratio of undecane to 1-chloroundecane only within experimental error.

A side reaction, however, which may affect the ratio of undecane to 1-chloroundecane is the hydrogen atom abstraction from the intermediate sigma

complexes which result in the formation of undecylated substrates (eq. 69). This side reaction may compete with the reaction under study (eq. 60). Even though the



eq. 69

concentration of the intermediate sigma complex is never greater than that of the undecylated aromatics (maximum 4%), the lability of the hydrogen in question might be orders of magnitude greater than that found in the substrates under investigation. This could be attributed to the re-aromatization of the system. In order to estimate an upper limit for the amount of undecane arising from the reaction described by equation 70, the following experiment was carried out. Lauroyl peroxide was allowed to decompose in an equimolar mixture of quinoline and carbon tetrachloride. The undecane to 1-chloroundecane ratio was monitored as a function of time. Quinoline was chosen for this study since it is the most prone of the parent systems utilized to undergo homolytic alkylation.[111] The ratios of undecane to 1-chloroundecane corresponding to different reaction times were determined by GLC and are shown in figure 10. Since a mixture of reactive undecylated quinolines is being formed, the undecane to 1-chloroundecane ratio must be extrapolated to zero time to obtain the inherent ability of the parent system to generate undecane. Extrapolation of the plot to zero time gave a value of 0.0014 ± 0.0002 for the inherent upper limit of undecane to 1-chloroundecane formed in this side reaction. It was found that this side reaction (eq. 69) can account for less that 4.5% of the undecane formed from toluene, the least reactive substrate studied. The corresponding value for the least reactive of the methylquinolines is under 2%. No correction was made since this maximum value is within the experimental error.

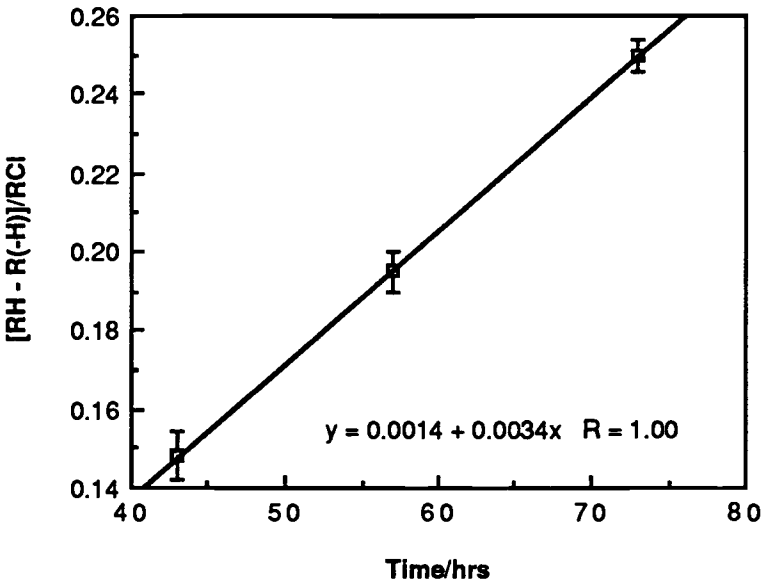


Figure 10. Ratio of undecane to 1-chloroundecane formed in the reaction of lauroyl peroxide with an equimolar mixture of quinoline and carbon tetrachloride versus time.

As regards extraneous undecane, the most serious source is that formed is the solvent cage by the disproportionation of undecyl radical (eq. 58). The disproportionation reaction yields an equimolar amount of undecane and 1-undecene. The amount of undecane formed by this reaction may be readily assessed by measuring the amount of 1-undecene formed. 1-Undecene was observed in nearly all of the systems investigated with the exception of 4-methylquinoline. 4-Methylquinoline was found to be the most reactive substrate among the compounds investigated toward hydrogen atom abstraction by undecyl radical. Under the reaction conditions utilized, no 1-undecene disappeared by undergoing addition with carbon tetrachloride. The product of the reaction, 1,1,1,3-tetrachlorododecane was independently synthesized and shown not to be present in the reaction mixtures. 1-Undecene might also arise

from similar disproportionaation between undecyl radical and dodecanoyloxy radical within the cage as shown below.

$$UnCO_2^{\bullet} + Un^{\bullet} \longrightarrow UnCO_2H + Un(-H) \qquad \text{eq. 70}$$

This process, however, must be minor as dodecanoic acid was not observed among the products in nearly all of the substrate studies. An exception was the 3-picoline case wherein a very small amount of dodecanoic acid was found. This material was present in about 1% of the undecane formed in the reaction. The relative reactivity of the homoaryl and heteroarylmethanes studied can now be determined using equation 71.

$$\frac{k_H}{k_{Cl}} = \frac{\text{Undecane-1-Undecene}}{\text{1-Chloroundecane}} \cdot \frac{[CCl_4]}{[QH]} \qquad \text{eq. 71}$$

The ratios of corrected undecane to 1-chloroundecane obtained for reaction of homoaryl and heteroarylmethanes with undecyl radical are presented in Table 8. The corresponding relative reactivities are found in Table 9, with toluene taken as reference compound. All compounds were run in replicate. Good precision was found for all systems (average standard deviation of 3.5%). A reactivity range of 15 was obtained. This is approximately double that found for hydrogen atom abstraction from the same series of compounds by tert-butoxyl radical.[99] Very substantial differences among positional isomers were found. In the homoarylmethane series; 1-methylnaphthalene was found to be 1.7 times more reactive than 2-methylnaphthalene, which was about 4 times more reactive than toluene. This same reactivity order has been found for the formation of carbocation,[112] carbanion[113] and radicals[92,99,114,115] at the benzylic position. In this respect,

Table 8. Corrected ratio of undecane to 1-chloroundecane obtained in the thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and homoaryl or heteroarylmethane at 70 °C.

System	$\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]^a}$	Number of runs
Toluene	0.031 ± 0.002[b]	5
3-Methylpyridine	0.033 ± 0.001	5
8-Methylquinoline	0.035 ± 0.002	5
3-Methylquinoline	0.082 ± 0.001	5
6-Methylquinoline	0.096 ± 0.004	5
7-Methylquinoline	0.096 ± 0.002	5
2-Methylnaphthalene	0.135 ± 0.003	5
2-Methylquinoline	0.184 ± 0.001	5
5-Methylquinoline	0.193 ± 0.004	3
1-Methylnaphthalene	0.228 ± 0.010	5
2-Methylpyridine	0.232 ± 0.020	5
4-Methylpyridine	0.347 ± 0.005	5
4-Methylquinoline	0.463 ± 0.018	5

[a] [QH] concentration of the homoaryl and heteroarylmethane.

[b] standard deviation

Table 9. Relative rates of hydrogen atom abstraction from homoaryl and heteroarylmethanes by undecyl radical at 70 °C.

System	k_{rel}	Number of runs
Toluene	1.00	5
3-Methylpyridine	0.07 ± 0.03[a]	5
8-Methylquinoline	0.13 ± 0.07	5
3-Methylquinoline	2.65 ± 0.03	5
6-Methylquinoline	3.10 ± 0.13	5
7-Methylquinoline	3.10 ± 0.07	5
2-Methylnaphthalene	4.36 ± 0.10	5
2-Methylquinoline	5.93 ± 0.03	5
5-Methylquinoline	6.23 ± 0.13	3
1-Methylnaphthalene	7.36 ± 0.32	5
2-Methylpyridine	7.48 ± 0.65	5
4-Methylpyridine	11.2 ± 0.16	5
4-Methylquinoline	14.9 ± 0.12	5

[a] standard deviation

our present results again significantly differ from those reported by Lissi et al.[116] Lissi et al. did not observe any difference among positions isomers in their reactivity toward hydrogen atom abstraction by tert-butoxy radical.[116] This discrepancy may be experimental in nature, as their workers refer to an "estimated error of ± 15%" in their data. Lissi et al. also carried out their reactions at 120 °C. This temperature is 50 °C higher than that employed in our studies.

In the heteroarylmethane systems, the introduction of electronegative nitrogen atom in the ring destroys the uniform pi electron distribution of the original hydrocarbon. As a result, the hydrogen donor ability of these substrates depends on the position of attachment of the methyl group to the ring. In the present work, the 2- and 4-methylpyridine were more reactive than the 3 isomer. The actual reactivities are as follow: 4-methylpyridine was 1.5 times more reactive than 2-methylpyridine, which in turn is 7 times more reactive than 3-methylpyridine. This is opposite to the trend observed in the reaction of these substrates with the electrophilic tert-butoxyl radical at 70 °C.[99] Nababsing has found that the reactivities of the methylpyridines towards hydrogen atom abstraction by the more electrophilic benzyl radical to be 2 > 3 > 4.[117] The reactivity order as found in the present work shows the importance of conjugative stabilization of the rate of formation of the heteroarylmethyl intermediates. This order of reactivity is also observed with the methylquinolines. For the substrates having the methyl group at positions that are in direct conjugation with the nitrogen atom, the order of reactivities found is 4 > 2 > 5 > 7. While for substrates bearing the methyl group at non-conjugated positions, the order of reactivities is 6 > 3 > 8. This is also opposite to the trend observed in the reaction of methyl quinolines with the electrophilic tert-butoxyl radical.[99] The results obtained in the present work emphasize the importance of the conjugative stabilization in the transition state of hydrogen atom

abstraction from homoaryl and heteroaryl methanes by the nucleophilic undecyl radical. This reactivity trend also suggests that partial negative charge is being developed in the transition state of hydrogen atom abstraction by undecyl radical.

It was already mentioned that the replacement of CH unit of an arene by an isoelectronic nitrogen atom destroys the uniform pi electron distribution of the parent system and changes the inductive characteristics of the heteroaryl group. Thus the parallelism of calculated energies for the benzylic carbocation, carbanion and radical derived from benzenoid hydrocarbon[96] is not found in the heteroarylmethyl intermdiates formed in the present study. The nature of the optimal theoretical correlation of the present results can provide some insight into the question of possible charge separation in the transition state of the reaction under study.

Correlations of the logarithms of relative rates of hydrogen atom abstraction from the series of homoaryl and heteroarylmethanes with the results of PMO[118] and HMO[119] calculations were not considered. Previous attempts to utilize PMO or HMO calculated quantities to correlate the relative rate of formation of heteroaryl intermediates gave poor results.[99,120] Thus, only correlations using a more advanced molecular orbital calcuations such as SCF-LCAO-MO approach[121-123] were attempted. For calculations on radicals, the suggestion of Pople and Nesbit[124] was adopted in keeping separate orbitals for electrons of opposite spins. The diagonal and off-diagonal matrix elements for an open shell SCF secular determinant are given in equations 73 and 74, respectively, for an electron of α-spin.

$$F^{\alpha}_{ii} = W_{2pi} + 1/2\, q^{\alpha}_{i}\,(ii,ii) + \sum_{i \neq j} (q^{\alpha}_{j} - C^{\alpha}_{j})\,(ii,jj) \qquad \text{eq. 72}$$

$$F^{\alpha}_{ij} = \beta_{ij} - p^{\alpha}_{ij}(ii,jj) \qquad \text{eq. 73}$$

W_{2p} is the ionization potential for an electron in a 2p orbital at atom i; 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 to be equal to the number of electrons donated by atom j to the pi system; (ii,jj) is the Coulomb integral between electrons centered on atoms i and j; (ii,ii) is the Coulomb integral between two electron centered on atom i; β_{ij} is the resonance integral for an electron in an orbital between atoms i and j. It is set equal to zero unless atoms i and j are bonded. p_{ij} is the bond order between atoms i and j. The core charge is set equal to 1/2 to account for the fact that only one-half of the electron is considered in a given matrix. The coefficient "one-half" has been removed from the second term of the traditional off-diagonal matrix element since all electrons considered in the present matrices can exchange. The resonance integrals were evaluated at each iteration by a thermocycle suggested by Dewar.[122,123]

SCF-PPP calculated total energy[125] differences between arylmethyl intermediates and starting materials, which were taken as being equivalent to the parent unmethylated system, were again used to evaluate the nature of any charge being developed in the transition state. The data for radical, carbocation and carbanion are respectively found in Tables 10, 11 and 12. Correlations based on carbocation and radical transition state were virtually nonexistent. The correlation coefficients were 0.51 and 0.10, respectively. A more reasonable correlation was obtained when arylmethyl carbanions were utilized to model the transition state. A correlation coefficient of 0.87 was obtained. The plot of the logarithms of relative rates for hydrogen atom abstraction from the series of substrates investigated against SCF calculated energy for a carbanion model is shown in Figure 11. Even though modest correlations were obtained, these results tend to support the formalism of substantial negative charge develpment in the transition state of the reaction under study. The results obtained are also in agreement with the idea that resonance form

IV described earlier is the major contributing form to the hybrid description of the transition state of benzylic hydrogen atom abstraction by a nucleophilic radical such as undecyl.

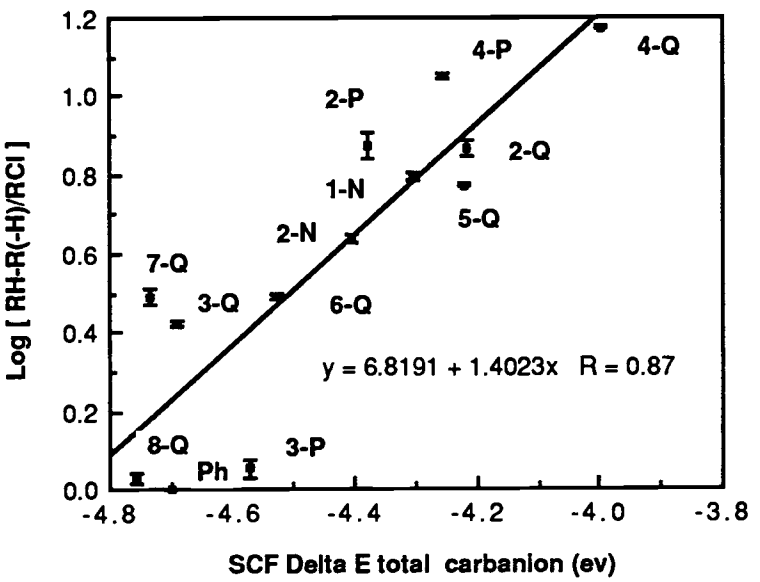


Figure 11. Logarithms of relative rates of hydrogen atom abstraction by undecyl radical from a series of homo and heteroarylmethane versus SCF calculated energy differences using a carbanion model.

Table 10. Relative SCF energy[a] differences between a series of aryl and heteroarylmethyl radicals and the parent arenes and heteroarenes.

	Parent Systems			Homo and Heteroarylmethyl Radical					
	E_π	E_σ[b]	E_T		E_π	E_σ[b]	E_T	ΔE_T	ΔE_π
Benzene	8.753	22.029	30.782		9.307	26.108	37.415	4.633	0.554
Napthalene	14.884	40.672	55.556	1 -	15.484	44.857	60.341	4.785	0.600
				2 -	15.422	44.812	60.234	4.678	0.538
Pyridine	9.592	20.998	30.590	2 -	10.126	25.007	35.133	4.543	0.534
				3 -	10.137	25.032	35.169	4.579	0.545
				4 -	10.130	25.019	35.149	4.559	0.538
Quinoline	15.699	39.643	55.644	2 -	16.242	43.639	59.881	4.237	0.543
				3 -	16.254	43.720	59.974	4.330	0.555
				4 -	16.281	43.713	59.994	4.350	0.582
				5 -	16.313	43.777	60.090	4.446	0.614
				6 -	16.275	43.737	60.012	4.368	0.576
				7 -	16.274	43.730	60.004	4.360	0.575
				8 -	16.313	43.782	60.095	4.451	0.614

[a] All energies in electron volts

[b] With bond length variation

Table 11. Relative SCF energy[a] differences between a series of aryl and heteroarylmethyl carbocations and the parent arenes and heteroarenes.

	Parent Systems			Homo and Heteroarylmethyl Carbocation					
	E_π	E_σ[b]	E_T		E_π	E_σ[b]	E_T	ΔE_T	ΔE_π
Benzene	8.753	22.029	30.782		11.326	25.889	37.215	6.433	2.573
Napthalene	14.884	40.672	55.556	1 -	17.896	44.569	62.465	6.909	3.012
				2 -	17.755	44.522	62.277	6.721	2.871
Pyridine	9.592	20.998	30.590	2 -	11.799	24.867	36.666	6.076	2.207
				3 -	12.229	24.850	37.079	6.489	2.637
				4 -	11.504	24.914	36.418	5.828	1.912
Quinoline	15.699	39.643	55.644	2 -	18.016	43.504	61.520	5.876	2.317
				3 -	18.601	43.463	62.064	6.420	2.902
				4 -	18.015	43.554	61.569	5.925	2.316
				5 -	18.569	43.513	62.082	6.438	2.870
				6 -	18.692	43.471	62.163	6.519	2.993
				7 -	18.467	43.493	61.960	6.316	2.768
				8 -	18.831	43.529	62.360	6.716	3.132

[a] All energies in electron volts

Table 12. Relative SCF energy[a] differences between a series of aryl and heteroarylmethyl carbanions and the parent arenes and heteroarenes.

	Parent Systems				Homo and Heteroarylmethyl Carbanion				
	E_π	E_σ[b]	E_T		E_π	E_σ[b]	E_T	ΔE_T	ΔE_π
Benzene	8.753	22.029	30.782		0.196	25.889	26.085	-4.697	-8.557
Napthalene	14.884	40.672	55.556	1 -	6.770	44.569	51.339	-4.217	-8.114
				2 -	6.627	44.522	51.149	-4.407	-8.257
Pyridine	9.592	20.998	30.590	2 -	1.454	24.576	26.210	-4.380	-8.138
				3 -	0.969	24.867	25.836	-4.754	-8.623
				4 -	1.586	24.749	26.335	-4.255	-8.006
Quinoline	15.699	39.643	55.644	2 -	8.026	43.399	51.425	-4.219	-7.673
				3 -	7.408	43.544	50.952	-4.692	-8.291
				4 -	8.202	43.446	51.648	-3.996	-7.497
				5 -	7.841	43.499	51.340	-4.304	-7.858
				6 -	7.401	43.508	50.909	-4.735	-8.298
				7 -	7.670	43.446	51.116	-4.528	-8.029
				8 -	7.541	43.531	51.072	-4.572	-8.158

[a] All energies in electron volts

[b] With bond length variation

Due to the modest nature of the correlations obtained utilizing energy differences, which imply a relatively late transition state, correlations using ground state parameters were considered. The charge density on the ring carbon attached to the methyl group was the chosen parameter. This is in keeping with Taylor's suggestion that charge density is the best parameter to correlate the reactivities of heterocyclic systems in reactions that do not involve an appreciable progress along the reaction coordinate.[100] The introduction of a nitrogen atom in the ring destroys the uniform pi electron density, which is no longer equal to unity as in alternant hydrocarbon. A poor correlation ($r = 0.60$) was obtained when the logarithms of relative rates of hydrogen atom abstraction by undecyl radical from the series investigated was plotted against charge densities. This does not completely exclude partial ground state control.

The results discussed so far suggest that the rate of hydrogen atom abstraction might be influenced by multiple factors. To test this hypothesis two approaches are considered.

a - Hydrogen atom abstraction by undecyl radical has a relatively early transition state. Thus, correlations should be based not only on energy changes, but should also include some ground state parameter.

b - It has been shown that hydrogen atom abstraction by undecyl radical exhibits polar character.[52] Therefore, any treatment of the transition state should reflect this radical-ionic dichotomy.

Four parameter equations of the form shown in equations 74 and 75 were developed by curve-fitting the kinetic data.

$$\text{Log } k_{rel} = a(\Delta E_T) + b \cdot q + c \qquad \text{eq. 74}$$

$$\text{Log } k_{rel} = a(\Delta E_T)_{anion} + b(\Delta E_T)_{rad} + c \qquad \text{eq. 75}$$

The values of the coefficients a, b and c were calculated using STATGRAPHICS version 2.6. The final equations obtained are as follows:

$$\text{Log } k_{rel} = 1.331(\Delta E_T)_{ani} - 0.335\ q + 6.828 \qquad \text{eq. 76}$$

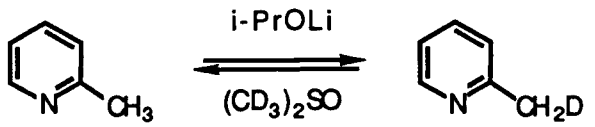
$$\text{Log } k_{rel} = 1.400(\Delta E_T)_{ani} - 0.165(\Delta E_T)_{rad} + 7.550 \qquad \text{eq. 77}$$

No improvement in the correlation (r = 0.85) was observed when the calculated logarithms of the relative ratio as calculated by either equation 76 or 77 were plotted against the logarithms of the experimental values. The radical-ion dichotomy discussed earlier implies a sizable contribution by both forms to the hybrid description of the transition state. Equation 77 indicates a very small contribution of structure II relative to structure IV to the transition state of hydrogen atom abstraction by undecyl radical.

Even though the correlations discussed so far are modest in nature, they tend to support the formation of partial negative charge development at the benzylic carbon in the transition state of hydrogen atom abstraction from homoaryl and heteroarylmethanes by undecyl radical.

Due to the modest nature of the correlations involving the rate data and calculated quantities, an attempt was made to correlate the relative rates of hydrogen atom abstraction with some comparable experimental results. This approach gave excellent results for hydrogen atom abstraction from the same series of homoaryl and heteroarylmethanes by tert-butoxyl radical.[99] Unfortunately, the amount of data in literature pertinent to the formation of heteroarylmethyl carbanion is rather

limited. One example, however, does exist. Shatenshtein and coworkers have reported the CH acidities of methylpyridines and several methylquinolines.[126] The kinetic CH acidities were obtained by the lithium isopropoxide catalyzed hydrogen-deuterium exchange of heteroarylmethanes in perdeuterodimethylsulfoxide.[126] Shatenshtein's results are listed in Table 13, and the reaction is shown below.



eq. 78

The base catalyzed hydrogen-deuterium exchange of carbon acid is well known to involve a carbanion intermediate.[127,123]

A fairly good correlation was obtained when the logarithms of the relative rates of hydrogen atom abstraction by undecyl radical were plotted against the corresponding logarithms of the kinetic CH acidities reported by Shatenshtein.[126] A correlation coefficient of 0.91 was obtained and the plot is shown in Figure 12. However, improved correlations were obtained when the series of heteroarylmethanes is divided into two sets: methylpyridines and methylquinolines. The correlation coefficients thus obtained were 0.97 and 0.95, respectively. The plots are shown in Figure 13 for methylpyridines and Figure 14 for methylquinolines. A justification for this is possible. Shatenshtein and coworkers have suggested that there are appreciable differences in the solvation of the carbanion intermediates derived from methylquinolines and methylpyridines.[126]

The homoarylmethanes studied could not be included in the correlation. Their acidities were determined under very different experimental conditions as regards solvent, temperature and base employed. An excellent correlation (r = 0.99) was

Table 13. Relative reactivities of methylquinolines and methylpyridine toward undecyl radical along with the corresponding kinetic CH acidities.

System	k_{rel} H-abstraction	$k \cdot 10^5$ sec^{-1} H/D exchange
2-Methylpyridine	1.38 ± 0.09	1.9 ± 0.2
3-Methylpyridine	1.12 ± 0.08	0.14 ± 0.01
4-Methylpyridine	1.43 ± 0.08	35 ± 2
2-Methylquinoline	3.49 ± 0.33	110 ± 10
3-Methylquinoline	2.92 ± 0.07	3.5 ± 0.2
4-Methylquinoline	5.08 ± 0.08	530 ± 60
5-Methylquinoline	3.43 ± 0.08	—
6-Methylquinoline	2.11 ± 0.08	1.2 ± 0.1
7-Methylquinoline	3.19 ± 0.04	1.1 ± 0.1
8-Methylquinoline	2.50 ± 0.04	0.14 ± 0.02

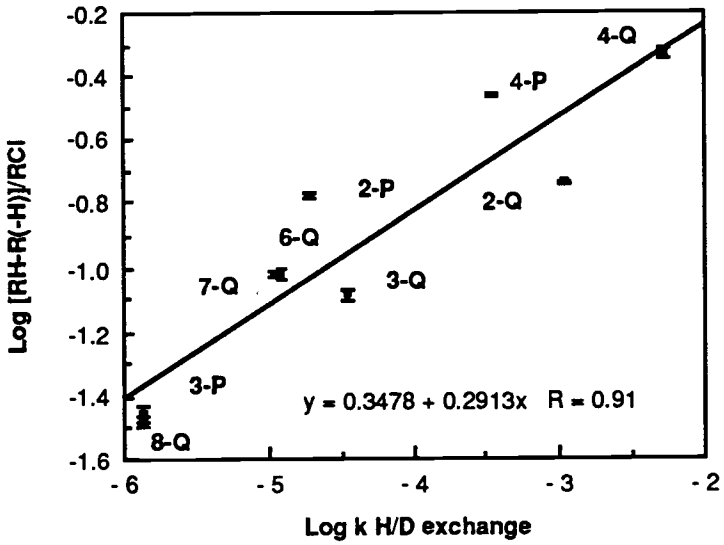


Figure 12. Logarithms of relative rates of hydrogen atom abstraction from methylquinolines and methylpyridines by undecyl radical versus the corresponding values for hydrogen deuterium exchange.

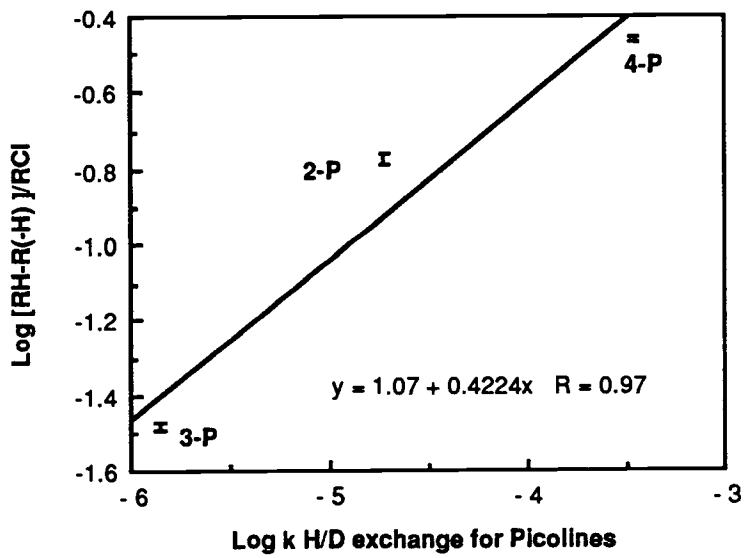


Figure 13. Logarithms of relative rates of hydrogen atom abstraction by methyl pyridines by undecyl radical versus the corresponding values for hydrogen-deuterium exchange.

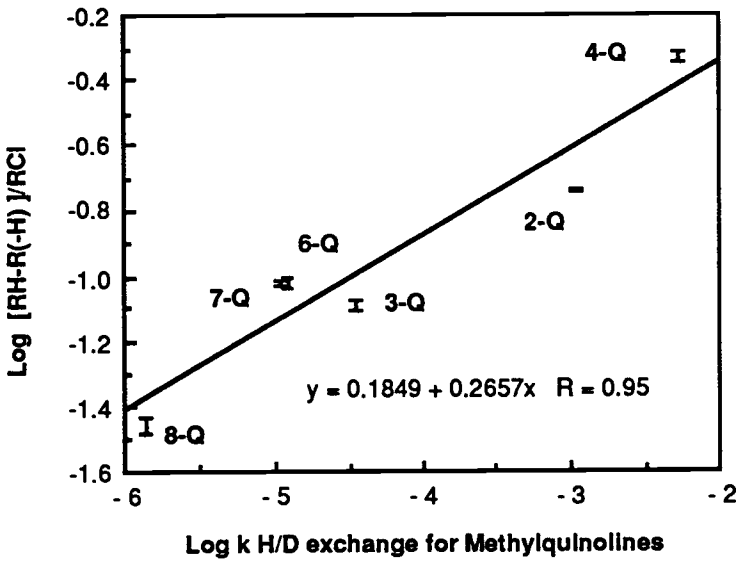


Figure 14. Logarithms of relative rates of hydrogen atom abstraction from methylquinolines by undecyl radical versus the corresponding values for hydrogen deuterium exchange.

obtained when the logarithms of the relative reactivities of the homoarylmethane studied towards undecyl radical were plotted against the corresponding logarithms of the kinetic CH acidities reported by Streitwieser.[129] The plot is shown in Figure 15.

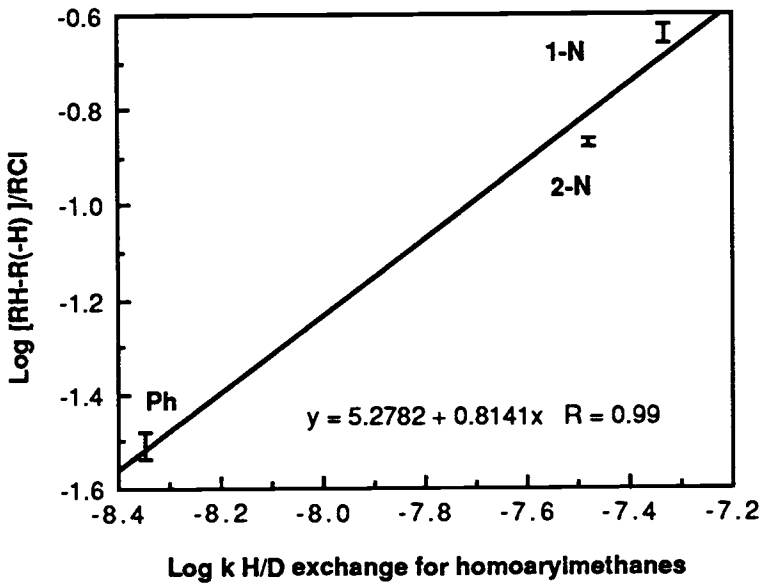


Figure 15. Logarithms of relative rates of hydrogen atom abstraction from homoarylmethanes by undecyl radical versus the corresponding values for hydrogen-deuterium exchange.

III. Relative Rates of Chlorine Atom Transfer from a Series of Heteroarylmethylchlorides to Triphenyltin Radical.

The relative rates for the reduction of the heteroarylmethylchlorides by triphenyltin hydride were obtained by direct competition with 1-chloro- methyl-naphthalene for a limiting amount of triphenyltin hydride. Solutions of the chosen heteroarylmethyl chloride, 1-chloromethylnaphthalene, α,α' bis(isoazo-butyro-nitrile), p-di-tert-butylbenzene, triphenyltin hydride and perdeutero-benzene were prepared in an approximate relative molar ratio of 10:10:1:1:5:600. These

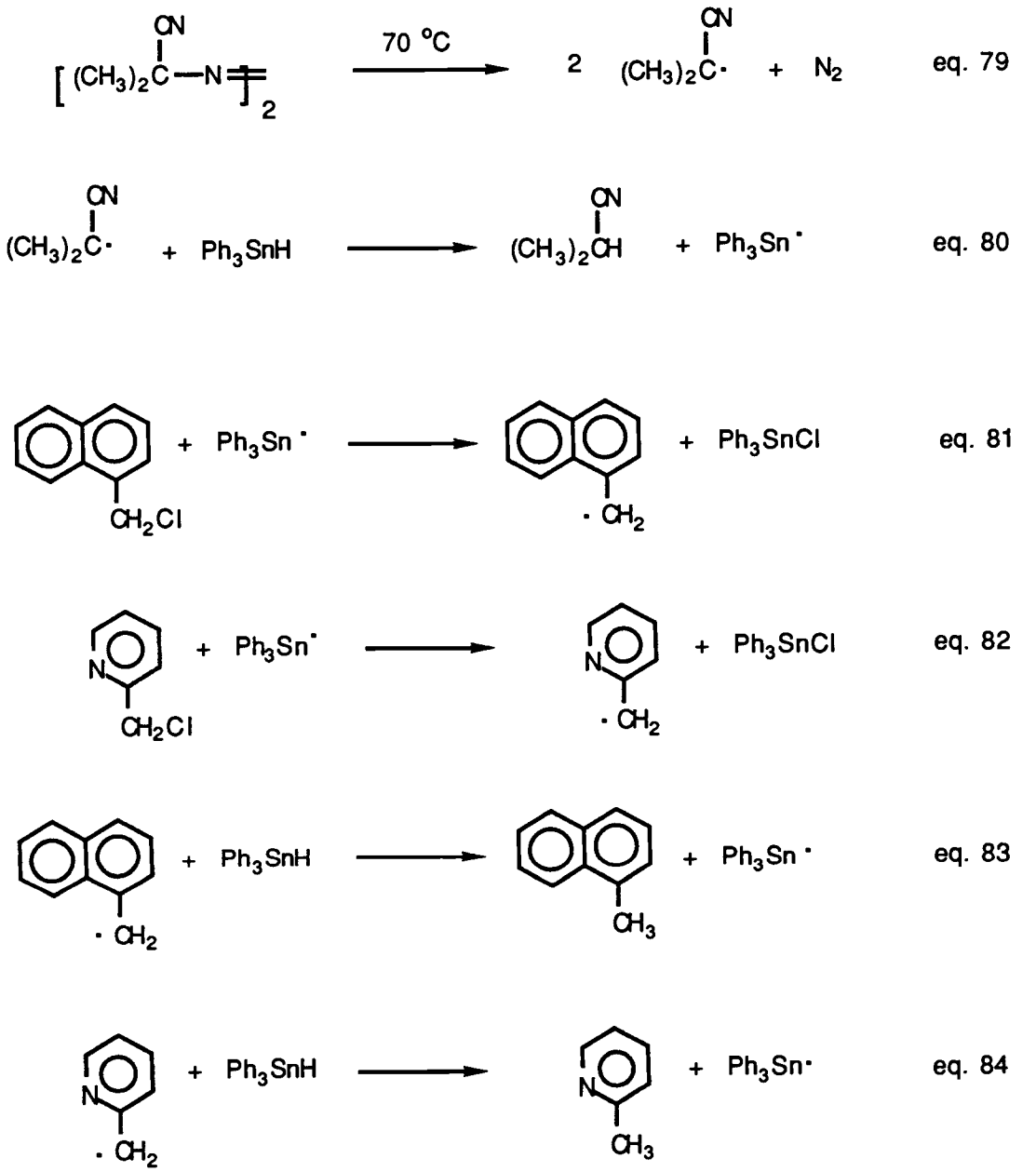
solutions were divided into several ampoules. After a series of freeze-thaw cycles, the ampoules were sealed under a reduced pressure of nitrogen and put in a constant temperature oil bath maintained at 70 ± 1 °C for 2 hours. Perdeuterobenzene was used as solvent to avoid strong solvent proton signals in the nmr analysis of the reaction mixture. Para di-tert-butylbenzene was present in the reaction mixture to function as an internal standard. Reaction progress was monitored by nuclear magentic resonance spectroscopy. The spectra were recorded on either a Bruker AM 400 or a Bruker AC 300 instrument.

The relative reactivities of the heteroarylmethyl chlorides to 1-chloromethylnaphthalene were obtained by a standard approach.[28] Using the internal standard p-di-tert-butylbenzene, the relative areas of the CH_2Cl signals in the reaction mixture were obtained and compared to those found in the starting material. Similarly, it is possible to obtain these relative reactivities from the relative amounts of heteroarylmethane to 1-methylnaphthalene formed in the reaction. The second approach was not considered in the present study. Prior investigations have shown excellent agreement between the two methods in the reaction of homoarylmethylchlorides,[103] oxygen containing heteroarylmethylchlorides[104] and polycyclic iodomethylarenes[79] with triphenyltin hydride.

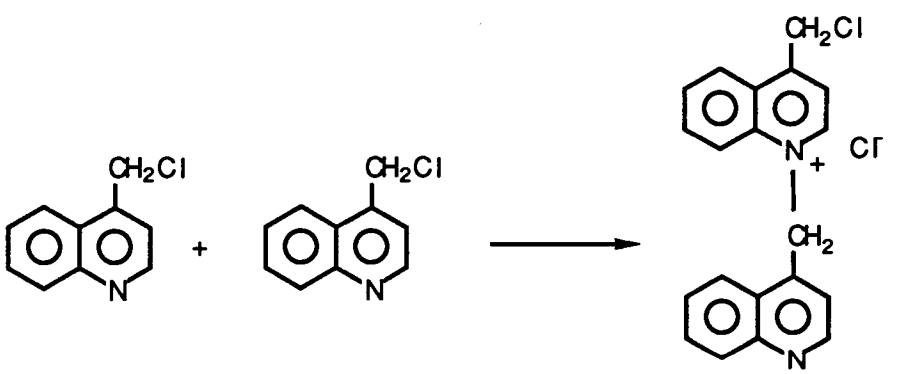
The generally accepted mechanism of the AIBN initiated reduction of heteroarylmethyl chlorides by triphenyltin hydride is shown in scheme 15 using 2-chloromethylpyridine as an example.

Before the rate of disappearance of the arylmethyl chlorides can be equated to the rate of chlorine atom transfer, it is necessary to make sure the disappearance of these compounds is due solely to chlorine atom abstraction. Tin radicals are known to add to alkenes[68a,7a,7b] and stannylation of the reactive sites in the aromatic portion of the substrate should be considered. However, triphenyltin radicals apparently

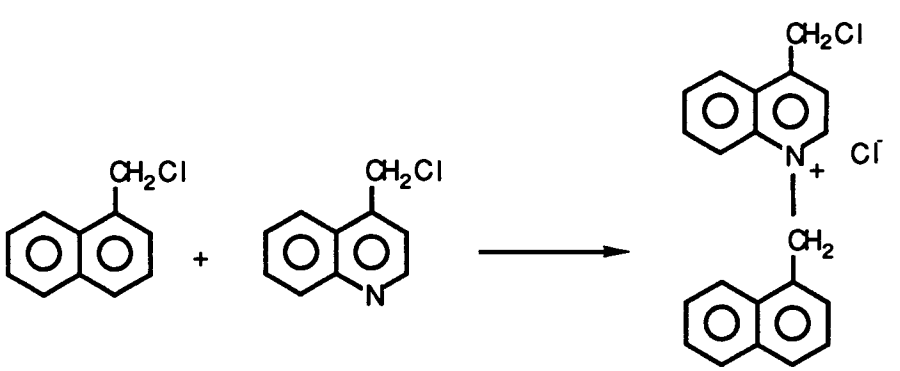
Scheme 15



have no tendency to add to the pyridine and quinoline rings. Gleicher and Soppe-Mbang[104] have shown that in a direct competition between benzyl chloride and pyridine, or anthracene, no reaction of the latter was observed even when 95% of the benzyl chloride has reacted. Ring stannylation does not seem to be a problem under our reaction conditions. Another possible route for disappearance of the chloromethylarenes is the reaction leading to quaternization of the ring nitrogen as shown in equations 85 and 86. However, in all the systems investigated no new signal corresponding to the CH_2 attached to the ring nitrogen was observed in the nmr. Furthermore, no appreciable change in the concentration of 4-chloromethylquinoline or 1-chloromethylnaphthalene was observed after standing for 24 hours at room temperature. This suggests that under our experimental conditions, the routes for disappearance of the chloromethylarenes depicted by equations 85 and 86 are not



eq.85

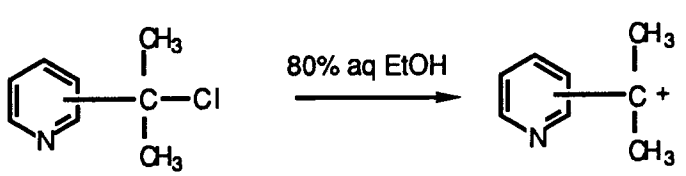


eq.86

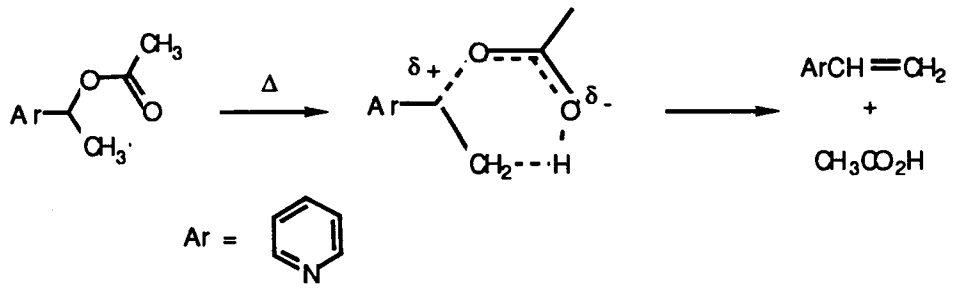
operative. Thus it is reasonable to assume that the only reaction taking place in the systems under investigation is the chlorine atom transfer.

The relative rates of disappearance of the heteroarylmethyl chlorides investigated to that of 1-chloromethylnaphthalene are listed in Table 14. Rates relative to benzyl chloride for the heteroaromatic systems are found in Table 15. Table 16 contains the values for the corresponding homoaromatic systems. All systems were run in replicate. A high precision was found for all systems. The average standard deviation found was under 4%. Even though the reactivity range between the most and the least reactive substrate studied was only a factor of 4.5, small differences among positional isomers are apparent. The relative rates for the chloromethylpyridines obtained in the present study are in reasonable agreement with those previously reported by Gleicher and Soppe-Mbang.[104]

The relative reactivities found for the three chloromethylpyridines is as follows: 4-pyridyl > 2-pyridyl > 3-pyridyl. These results parallel those obtained for hydrogen by the nucleophilic undecyl from the methylpyridine. These results are also opposite to those reported by Noyce and coworkers for the solvolysis at 2-(pyridyl)-2-chloropropanes[129] which is shown in equation 87. They are also opposite to those obtained by Taylor[102] for the pyrolysis of 1-(pyridyl)ethyl acetates shown in equation 88. These latter reactions, which are known to involve an appreciable carbocation character at the benzylic carbon in their respective transition states, show the 3-pyridyl isomers to be the most reactive. This suggests that there is an appreciable negative charge development at the benzylic carbon in the transition state of chlorine atom transfer from chloromethylpyridines to



eq. 87



eq. 88

triphenyltin radical. The difference observed in order of reactivity between cationic and anionic like processes reflect again the inductive properties of the nitrogen heteroatom.

Table 14. Relative rates of disappearance of heteroarylmethyl chlorides vs. 1-chloromethylnaphthalene.

System	Log k_{rel}	Number of runs
3-Chloromethylpyridine	0.34 ± 0.02[a]	4
2-Chloromethylpyridine	0.42 ± 0.03	4
4-Chloromethylpyridine	0.43 ± 0.02	4
6-Chloromethylquinoline	0.64 ± 0.02	4
8-Chloromethylquinoline	0.76 ± 0.01	5
3-Chloromethylquinoline	0.89 ± 0.02	4
7-Chloromethylquinoline	0.97 ± 0.01	4
5-Chloromethylquinoline	1.04 ± 0.02	4
2-Chloromethylquinoline	1.06 ± 0.10	4
4-Chloromethylquinoline	1.54 ± 0.08	5

[a] Standard deviation

Table 15. Relative rates of chlorine atom transfer from heteroarylmethyl chlorides to triphenyltin radical.

System	k_{rel}[a]
3-Chloromethylpyridine	1.12 ± 0.08[b]
2-Chloromethylpyridine	1.38 ± 0.09
4-Chloromethylpyridine	1.43 ± 0.08
6-Chloromethylquinoline	2.11 ± 0.08
8-Chloromethylquinoline	2.50 ± 0.04
3-Chloromethylquinoline	2.92 ± 0.07
7-Chloromethylquinoline	3.19 ± 0.04
5-Chloromethylquinoline	3.43 ± 0.07
2-Chloromethylquinoline	3.49 ± 0.33
4-Chloromethylquinoline	5.08 ± 0.08

[a] Benzyl chloride is taken as the reference compound

[b] Standard deviation

Table 16. Relative rates[a] of chlorine atom transfer from homoarylmethyl chloride to triphenyltin radical at 70 °C.

System	k_{rel}
Benzyl chloride	1.00
2-Chloromethylnaphthalene	1.88 ± 0.11
1-Chloromethylnaphthalene	3.29 ± 0.48

[a] Taken from reference 104

For the chloromethylquinoline isomers, the reactivity order obtained is as follows: 4-Q > 2-Q > 5-Q > 7-Q > 3-Q > 8-Q > 6-Q. The chloromethylquinoline isomers having the chloromethyl group at positions in direct conjugation with the nitrogen atom (2,4,5,7-chloromethylquinoline) are more reactive than those having the reaction site in positions where this direct conjugation is not possible. These results suggest again the importance of the conjugative resonance stabilization in the transition state of chlorine atom transfer from heteroarylmethyl chlorides to the nucleophilic triphenyltin.

In order to bring some insight into the question of possible charge separation in chlorine atom transfer, correlations of the logarithms of the relative rates with SCF[125] calculated energy differences between the appropriate arylmethyl intermediate (carbocation, carbanion or radical) and starting materials, which were taken as being equivalent to that of the parent, unsubstituted system[99,103,104] were carried out. The data for carbocation, carbanion and radical transition states are

respectively found in Tables 11, 12 and 10. The results obtained for the various correlations attempted are summarized in Table 17.

One of the goals of the present work was to treat both homocyclic and heterocyclic systems in a single correlation. The results of the correlations based on the standard energy difference approach are found in Table 17, entries 1-6. Although the correlation coefficients found are rather low, optimum correlations were obtained when a carbanion model was utilized to model the transition state of the reaction under study. This would seem to indicate that appreciable negative charge builds up in the transition state. The correlations based on a cationic model for the intermediate are particularly poor. No further use of this model is made.

It should be noted, however, that these correlations are based on a relatively late transition state. It would be interesting to investigate whether other factors might play a significant role in determining the relative rates of chlorine atom transfer. Two approaches were considered. Chlorine atom transfer to nucleophilic tin radical has been shown to have polar character,[70,71,73] thus any treatment of the transition state should reflect this radical vs. ionic dichotomy. Also, since chlorine atom transfer has been shown to occur at a relatively early stage, a correlation including not only energy differences (late transition state-parameter) but also a ground-state parameter might be in order. Charge densities were utilized as the ground-state parameter in keeping with Taylor's suggestion[100] that it is the best parameter to correlate the reactivities of heterocyclic systems in reactions that involve an early transition state.

Table 17. Correlation of logarithms of relative rates of chlorine atom transfer from homoaryl and heteroarylmethyl chlorides to triphenyltin radical.

Entry	Parameters	Correlation Coefficient			
		All Points[b]	All Heteroaryl	Quinolines	Pyridines
1.	Pi energy carbocation	0.25	0.23	0.82	0.98
2.	Pi energy carbanion	0.79	0.76	0.90	1.00
3.	Pi energy radical	0.57	0.54	0.04	0.88
4.	Total energy carbocation	0.06	0.11	0.78	0.97
5.	Total energy carbanion	0.57	0.48	0.91	0.99
6.	Total energy radical	0.51	0.81	0.26	0.83
7.	Charge densities	0.15	0.12		
8.	Pi energy carbanion and radical	0.85	0.80	0.85	1.00
9.	Pi energy carbanion and charge densities	0.89	0.86	0.92	1.00
10.	Pi energy radical and charge densities	0.58	0.51	0.00	1.00
11.	Total energy carbanion and radical	0.69	0.84	0.87	1.00
12.	Total energy carbanion and charge densities	0.53	0.40	0.90	1.00
13.	Total energy radical and charge densities	0.33	0.75	0.00	1.00

[a] SCF calculated parameters

[b] Homoarylmethyl chlorides from reference 104 were included

For testing the above approaches, four-parameter equation of the form shown in equations 89 and 90 were developed by multilinear regression.

$$\text{Log } k_{rel} = a \cdot \Delta E + b \cdot q + c \qquad \text{eq. 89}$$

$$\text{Log } k_{rel} = a(\Delta E)_{anion} + b(\Delta E)_{radical} + c \qquad \text{eq. 90}$$

It should be noted that these equations are similar in principle to that proposed by Yukawa and Tsuno for Hammett correlation which would reflect the sensitivity of transition state to both radical and ionic factors.[130]

The results of correlations of the calculated logarithms of relative rates of chlorine atom transfer using equations 89 and 90 are found in Table 17, entries 8-13.

Even though all correlations were improved, better results were obtained when pi energy, rather than total energy differences, were employed. No rationale can be provided for this observation. Optimum results were obtained from an equation utilizing anion intermediate pi energy changes and charge densities. The equations developed for all systems (homoarylmethyl and heteroarylmethyl chlorides), heteroarylmethyl chlorides (quinolines and pyridine) and just the chloromethylquinolines are shown in equations 91, 92 and 93.

$$\text{Log } k_{rel} = 0.796 \cdot \Delta E_{\Pi anion} + 1.589 \cdot q + 5.276 \qquad \text{eq. 91}$$

$$\text{Log } k_{rel} = 0.746 \cdot \Delta E_{\Pi anion} + 1.454 \cdot q + 5.005 \qquad \text{eq. 92}$$

$$\text{Log } k_{rel} = 0.501 \cdot \Delta E_{\Pi anion} + 0.683 \cdot q + 3.829 \qquad \text{eq. 93}$$

The plots of the logarithms of the calculated relative rates using equations 91-93 against their experimental counterparts are shown in figures 16, 17 and 18, respectively.

A most interesting finding in the utilization of equations 89 and 90 is the poorer nature of correlations incorporating radical intermediate energy changes with other parameters. It should be noted that the worst approach is that which completely ignores charge separation in the transition state (entries 10 and 13, Table 17).

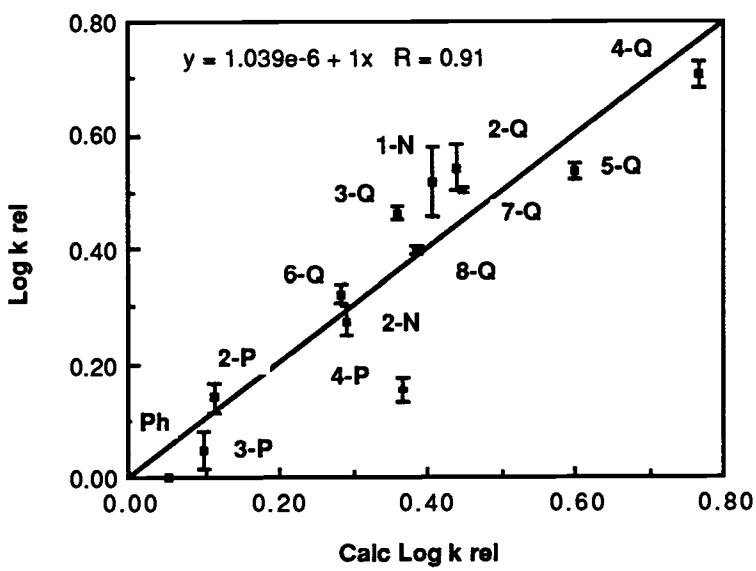


Figure 16. Logarithms of the relative rates of chlorine atom transfer from homoarylmethyl and heteroarylmethyl chlorides to triphenyltin radical versus logarithms of the calculated relative rates using a four parameter equation $\Delta E_{\Pi anion}$ and q.

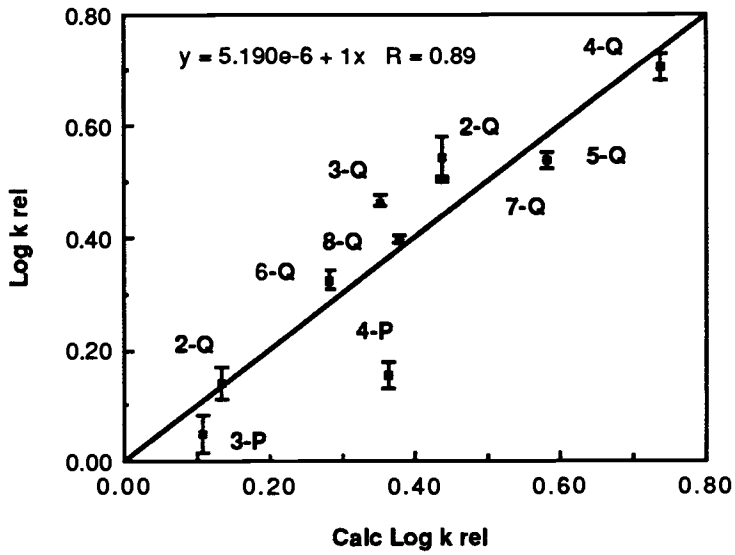


Figure 17. Logarithms of the relative rates of chlorine atom transfer from heteroarylmethyl chlorides by triphenyltin radical versus logarithms of the calculated relative rates using a four parameter equation $\Delta E_{\Pi anion}$ and q.

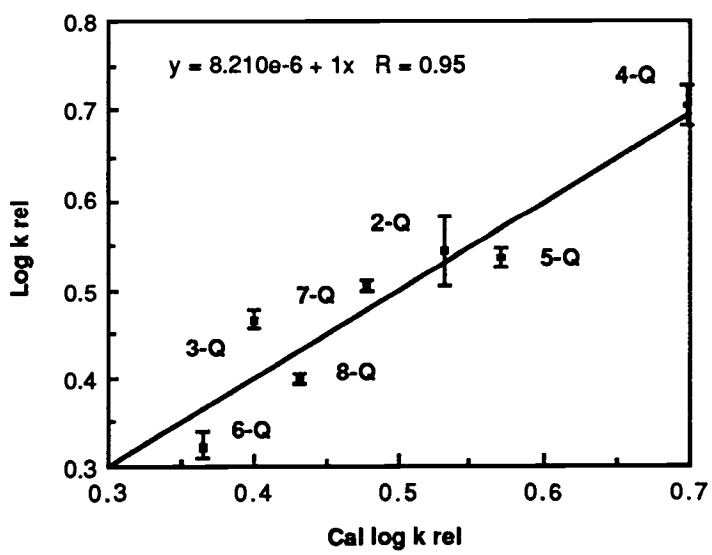


Figure 18. Logarithms of the relative rates of chlorine atom transfer from chloromethylquinolines to triphenyltin radical versus logarithms of the calculated relative rates using a four parameter equation $\Delta E_{\Pi anion}$ and q.

The correlations discussed so far are only modest in their nature. They do, however, tend to support the idea that the transition state in the rate determining step of chlorine atom transfer to nucleophilic tin radicals is polar and may occur at a relatively early stage as discussed above.

Poor results were also obtained when the logarithms of the relative rates of chlorine atom transfer were plotted against their counterparts for hydrogen atom abstraction from the corresponding homoaryl and heteroarylmethanes by the undecyl radical discussed earlier. The correlation coefficient was 0.53.

These poor correlations suggest that the rate determining step may not involve direct atom abstraction. A key observation leading to this conclusion is the decreased dependence of reactivity on positional factors. The seven chloromethylquinolines, for example, show a reactivity range of only ca. 2.5. The seven corresponding methylquinolines showed a range of ca. 13.5 in hydrogen atom abstraction by the undecyl radical. Hammett studies on the reaction of substituted benzyl chlorides with tributyltin radical[73] and substituted toluenes with undecyl radical[52] suggest that the former should be the inherently more selective system.

The literature contains previous reports on possible electron transfer involvement in the rate determining step of halogen atom transfer[74,79] and germanyl radicals.[76] If chlorine atom transfer from homoarylmethyl and heteroarylmethyl chlorides to the nucleophilic triphenyltin radical involves an electron transfer in the rate determining step, LUMO energies might be a reasonable parameter to correlate the relative reactivities obtained in this investigation.

The averages of the logarithms of relative rates of chlorine atom transfer for each parent system and SCF-PPP[126] LUMO energy difference between the parent unsubstituted systems and benzene are listed in Table 18.

Table 18. Averages of the relative rates of chlorine atom transfer and relative LUMO energies of the parent systems.

System	Average[a] k_{rel}	Log Average k_{rel}	ΔE_{LUMO}[b]
Benzene	1.00	0.00	0.00
Pyridine	1.31 ± 0.17[c]	0.12 ± 0.05	-0.45
Naphthalene	2.59 ± 1.00	0.41 ± 0.15	-0.86
Quinoline	2.87 ± 1.47	0.46 ± 0.18	-1.18

[a] Obtained by averaging the relative rates of positional isomers

[b] SCF-PPP calculated LUMO energies

[c] Standard deviation

The correlation between these data was excellent. A correlation coefficient of 0.99 was obtained. The plot is shown in Figure 19.

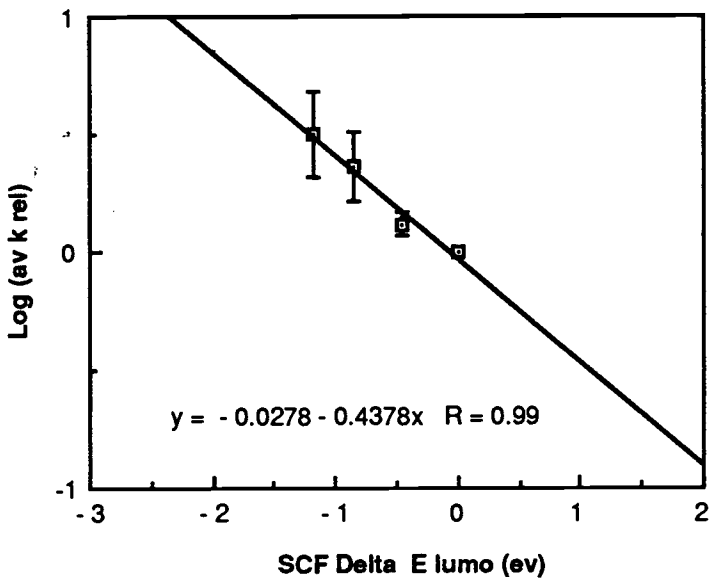


Figure 19. Logarithms of average relative rates of chlorine atom transfer to triphenyltin radical versus relative LUMO energy of the parent systems.

In order to take into account the small, but probably real, positional dependence which is observed, four-parameter equations of the form shown in equations 94 and 95 were developed by curve fitting the experimental data.

$$\text{Log } k_{rel} = a \cdot \Delta E_{LUMO} + b \cdot \Delta E + c \qquad \text{eq. 94}$$

$$\text{Log } k_{rel} = a \cdot \Delta E_{LUMO} + b \cdot q + c \qquad \text{eq. 95}$$

ΔE_{LUMO} is the LUMO energy difference between the parent unsubstituted system and benzene. This energy should not appreciably differ among positional isomers. The

results of correlations of the calculated logarithms of relative rates with their experimental counterparts are summarized in Table 19.

Table 19. Correlations[a] of logarithms of relative rates of chlorine atom transfer from homoarylmethyl and heteroarylmethyl chlorides to triphenyltin radical.

Entry	Parameters	Correlation coefficient	
		All points	Heteroaromatic systems only
1.	Pi energy radical and ΔE_{LUMO}	0.854	0.837
2.	Pi energy anion and ΔE_{LUMO}	0.949	0.965
3.	Total energy radical and ΔE_{LUMO}	0.847	0.848
4.	Total energy anion and ΔE_{LUMO}	0.962	0.970
5.	Charge densities and ΔE_{LUMO}	0.864	0.837

[a] For equations see Appendix

Much better correlations are obtained. This is especially true when carbanion intermediate energy changes were utilized along with the LUMO energy differences. The equations obtained are shown below. The correlation coefficients obtained when

$$\text{Log } k_{rel} = 0.297\ \Delta E_{\Pi anion} - 0.336\ \Delta E_{LUMO} + 2.475 \qquad \text{eq. 96}$$

$$\text{Log } k_{rel} = 0.354\ \Delta E_{Tanion} - 0.421\ \Delta E_{LUMO} + 1.563 \qquad \text{eq. 97}$$

pi or total energy changes are utilized are 0.929 and 0.942 respectively. Table 20 contains the values of the relative rates as calculated by equations 96 and 97. These calculated values are, on the average, within 13 percent of their experimental counterparts. The plots of experimental vs. calculated logarithms of relative rates are shown in figures 21 and 22. It should be noted that extremely poor results were found for double correlations that ignore charge separation in the transition state.

Table 20. Calculated relative rates of chlorine atom transfer from homoaryl and heteroarylmethyl chlorides to triphenyltin radical.

Systems	experimental k_{rel}	calculated k_{rel} from	
		eq. 97	eq. 96
2-Chloromethylpyridine	1.38 ± 0.09	1.59	1.61
3-Chloromethylpyridine	1.12 ± 0.08	1.17	1.15
4-Chloromethylpyridine	1.43 ± 0.08	1.75	1.76
2-Chloromethylquinoline	3.49 ± 0.33	3.67	3.89
3-Chloromethylquinoline	2.92 ± 0.07	2.49	2.55
4-Chloromethylquinoline	5.08 ± 0.08	4.40	4.39
5-Chloromethylquinoline	3.43 ± 0.07	3.42	3.43
6-Chloromethylquinoline	2.11 ± 0.08	2.41	2.54
7-Chloromethylquinoline	3.19 ± 0.04	2.75	3.05
8-Chloromethylquinoline	2.50 ± 0.04	2.75	2.79
Toluene	1.00	0.79	0.85
1-Chloromethylnaphthalene	3.29 ± 0.48	2.69	2.25
2-Chloromethylnaphthalene	1.88 ± 0.11	2.31	2.04

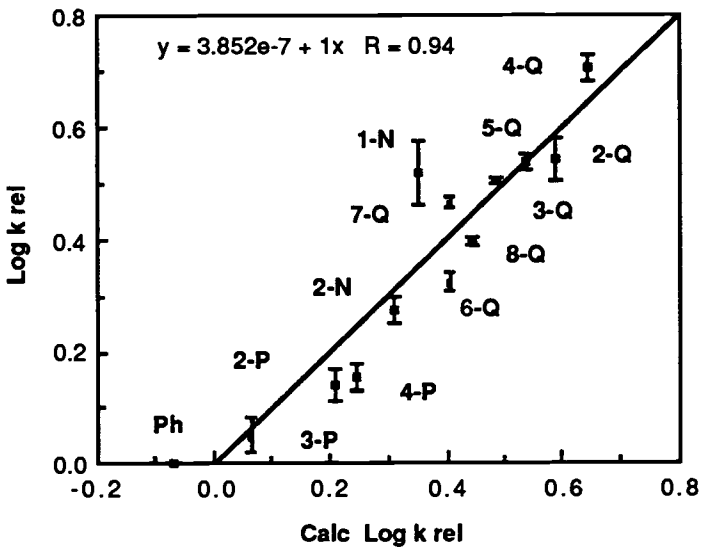


Figure 20. Logarithms of relative rates of chlorine atom transfer from homoarylmethyl and heteroarylmethyl chlorides to triphenyltin radical versus logarithms of calculated relative rates using a four parameter equation $\Delta E_{\Pi anion}$ and ΔE_{LUMO}.

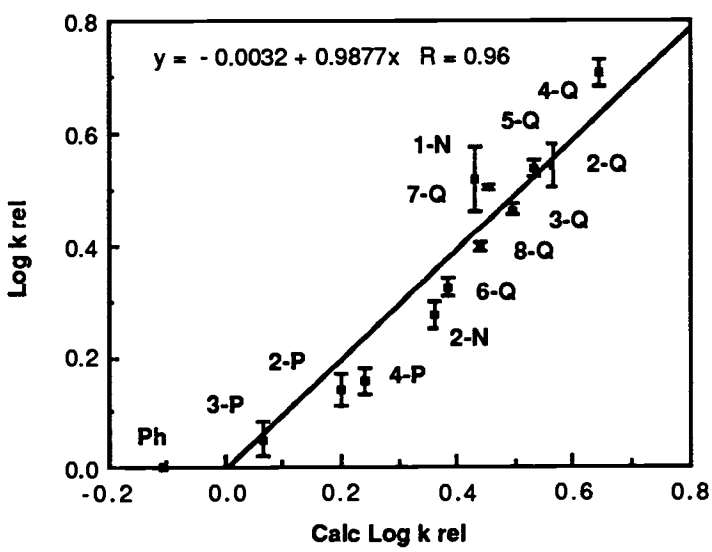


Figure 21. Logarithms of relative rates of chlorine atom transfer from homoarylmethyl and heteroarylmethyl chlorides to triphenyltin radical versus logarithms of calculated relative rates using a four parameter equation ΔE_{Tanion} and ΔE_{LUMO}.

The results obtained from the use of either equation 96 or 97; the poor correlations found when direct atom abstraction is considered; and, finally, the small range of reactivities are suggestive of electron transfer involvement in the rate determining step of chlorine atom transfer from the present homoarylmethyl and heteroarylmethyl chlorides by triphenyltin radical. The rate determining steps which might be operative are shown below.

$$ArCH_2Cl + {}^{\bullet}SnPh_3 \longrightarrow ArCH_2Cl\rceil^{\bullet-}\ \overset{+}{S}nPh_3 \qquad \text{eq.98}$$

$$ArCH_2Cl\rceil^{\bullet-}\ \overset{+}{S}nPh_3 \longrightarrow Ar\overset{\bullet}{C}H_2 + Ph_3SnCl \qquad \text{eq.99}$$

The first step (eq. 98) involves an electron transfer from the electropositive tin atom to the LUMO of the substrate, followed by chloride atom loss in the second step (eq. 99). Correlations resulting from the use of equations 94 or 95 could reflect the contribution of resonance forms A and B to the hybrid description of the transition state

$$\underset{A}{R-Cl\rceil^{\bullet-}\ \overset{+}{S}nPh_3} \longleftrightarrow \underset{B}{R{:}^{-}\ \overset{\bullet}{C}l\ \ \overset{+}{S}nPh_3} \longleftrightarrow \underset{C}{R^{\bullet}\ {:}^{-}Cl\ \ \overset{+}{S}nPh_3}$$

The coefficient of carbanion intermediate energy change and that of the LUMO energy are a measure of the importance of resonance forms A and B respectively.

EXPERIMENTAL

Gas-liquid chromatographic analysis was carried out with either a Varian 3300 or Varian 3400 capillary gas chromatograph equipped with an FID detector, 30 m x 0.25 mm DB-5 capillary column and a Varian 4290 integrator. Helium was the carrier gas. Melting points were measured with a Buchi melting point apparatus. Boiling points and melting points are uncorrected. Nuclear magnetic resonance spectra were recorded on a Bruker AM-400 or Bruker AC-300 instrument using tetramethylsilane as a reference and deuteriochloroform or perdeuteriobenzene as solvent.

Purification of Reagents

The purity of the reagents was determined by gas chromatography and was better than 99% in all cases. The purification methods and the literature data for physical properties were taken from "Purification of Laboratory Chemicals."[131]

Purification of acetone. Spectrophotometry grade acetone was dried over anhydrous potassium carbonate then distilled onto 4A Linde molecular sieves and kept under a nitrogen atmosphere.

Purification of methanol. Spectrophotometry grade methanol was dried over 4A Linde molecular sieves and used without further purification.

Purification of benzene. Reagent grade benzene (Baker) was washed three times with one-tenth of its volume of concentrated sulfuric acid, then washed with water and 5% sodium carbonate solution. After a final wash with water, the benzene was dried over magnesium sulfate and distilled onto calcium hydride. The benzene was then stirred overnight over calcium hydride and distilled onto 4A Linde molecular sieves. It was kept under an inert atmosphere of nitrogen.

Purification of perdeuteriobenzene. Perdeuteriobenzene 99.5 atom% D (Aldrich) was stored over 4A Linde molecular sieves under nitrogen. It was used without further purification.

Purification of quinoline. Reagent grade quinoline (Aldrich) was dried over magnesium sulfate for two days. It was then refluxed over barium oxide for 12 hours and distilled onto zinc powder. The quinoline was then fractionally vacuum distilled from the zinc powder onto 4A Linde molecular sieves. The fraction boiling at 92-93 at 10 torr was collected and kept under nitrogen (lit. 111.5 °C/16 torr).

Purification of carbon tetrachloride. To spectrophotometry grade carbon tetrachloride (Baker) was added its volume of 10 M aqueous potassium hydroxide. The two phase mixture was vigorously stirred for 24 hours. After separation, the organic layer was dried over calcium chloride and was distilled from phosphorus pentoxide onto 4A Linde molecular sieves. Storage was under nitrogen.

Purification of chlorobenzene. Reagent grade chlorobenzene (Aldrich) was washed three times with one-tenth of its volume of concentrated sulfuric acid. The temperature was kept below 20 °C. It was then washed with water and a 5% solution of sodium bicarbonate. After drying over magnesium sulfate it was distilled under nitrogen. The fraction boiling at 132-133 °C (lit. 131.7) was collected and stored over 4A Linde molecular sieves under a nitrogen atmosphere.

Purification of p-di-tert-butylbenzene. Commercial p-di-tert-butylbenzene (Aldrich) was recrystallized twice from diethylether and dried under vacuum. M.p. 76-77 °C (lit. 76-77.5 °C).

Purification of α,α' azobisisobutyronitrile. Commercial α,α' azobisisobutyronitrile (Aldrich) was recrystallized from chloroform below 40 °C by addition of petroleum ether. It was then dried under vacuum and stored in a brown

glass bottle under refrigeration. M.p. 101.5-102 °C with decomposition (lit. 103 °C).

Purification of triphenyltin hydride. Reagent grade triphenyltin hydride (Aldrich) was kept in a freezer and used without further purification.

Purification of toluene. Reagent grade toluene (Baker) was washed three times with one-tenth of its volume of concentrated sulfuric acid. The temperature was kept below 20 °C. It was washed with water and 5% sodium bicarbonate solution. After drying over calcium chloride, it was distilled onto calcium hydride. It was then fractionally distilled under nitrogen onto 4A Linde molecular sieves. The fraction boiling at 110 °C was collected and kept under argon.

Purification of 2-methylpyridine. Reagent grade 2-methylpyridine (Reilly Tar & Chemical) was fractionally distilled under nitrogen and the fraction boiling at 126-128 °C was collected. To this fraction was added one-tenth of its volume of 20% sulfuric acid solution. This mixture was steam distilled to remove the hydrocarbons. About 15% of the 2-methylpyridine also distilled over. The remaining material was basified by addition of sodium hydroxide pellets. After separation, the aqueous layer was extracted with three portions of ether. The organic layers were combined and dried over magnesium sulfate for a day. After evaporation of the ether solvent it was distilled from barium oxide onto zinc powder. It was finally fractionally distilled from the zinc powder under nitrogen onto 4A Linde molecular sieves. The fraction boiling at 127-128 °C (lit. 129.5 °C) was collected and kept under nitrogen.

Purification of 3-methylpyridine. Reagent grade 3-methylpyridine (Reilly Tar & Chemical) was purified according to the method described for 2-methylpyridine. The fraction boiling at 142-142.5 °C (lit 144 °C/767 torr) was collected and stored over 4A Linde molecular sieves under an inert atmosphere of nitrogen.

Purification of 4-methylpyridine. Reagent grade 4-methylpyridine (Aldrich) was purified by the method described for 2- and 3-methylpyridine. The fraction boiling at 145-146 °C was collected and stored over 4A Linde molecular sieves under nitrogen (lit. 144 °C/765 torr).

Purification of 1-methylnaphthalene. Reagent grade 1-methylnaphthalene (Milwaukee) was dried over calcium chloride and distilled under vacuum. The fraction boiling at 92-94 °C at 8 torr was collected. It was then fractionally distilled under vacuum from barium oxide onto 4A Linde molecular sieves. The fraction boiling at 93-94 °C at 8 torr was collected and kept under argon (lit. 244.6 °C).

Purification of 2-methylnaphthalene. Commercial 2-methylnaphthalene (Aldrich) was fractionally distilled under vacuum with the fraction boiling at 91-92 °C at 18 torr being collected. It was then recrystallized twice from absolute methanol and then dried in an Aberhalden pistol. M.p. 34.5 °C (lit. 34.7-34.9 °C).

Purification of 2-methylquinoline. 2-Methylquinoline (Aldrich) was refluxed over barium oxide overnight, then distilled under vacuum onto zinc powder. It was then fractionally distilled under vacuum from the zinc powder onto 4A Linde molecular sieves. The fraction boiling at 79-80 °C at 2 torr was collected and kept under argon (lit. 246-247 °C).

Purification of 3-methylquinoline. 3-Methylquinoline (Aldrich) was used without further purification.

Purification of 4-methylquinoline. 4-Methylquinoline (Aldrich) was dried over granular magnesium sulfate overnight. It was then refluxed over barium oxide for 12 hours and distilled onto zinc powder. It was then fractionally distilled under vacuum onto 4A Linde molecular sieves. The fraction boiling at 92-92.5 °C at 1 torr was collected and stored under nitrogen (lit. 265.5 °C).

Purification of 6-methylquinoline. 6-Methylquinoline from Aldrich was refluxed over barium oxide for 12 hours, then distilled onto zinc powder. It was fractionally distilled under vacuum from the zinc powder onto 4A Linde molecular sieves. The fraction boiling at 72 °C at 0.5 torr was collected and kept under nitrogen (lit. 258 °C).

Purification of 7-methylquinoline. 7-Methylquinoline from Aldrich was distilled under vacuum from zinc powder. The fraction boiling at 77-78 °C at 2 torr was collected and used immediately (lit. 255-260 °C).

Purification of 8-methylquinoline. 8-Methylquinoline (Aldrich) was refluxed over barium oxide for 12 hours, then distilled under vacuum onto zinc powder. It was then fractionally distilled and the fraction boiling at 71 °C at 1.5 torr was collected and kept under nitrogen (lit. 247.8 °C).

Purification of 2- and 4-chloromethylpyridine hydrochloride salts. The 2- and 4-chloromethylpyridine hydrochloride salts (Aldrich) were used without further purification.

Purification of 1-chloromethylnaphthalene. Reagent grade 1-chloromethylnaphthalene (Aldrich) was dried over sulfate then fractionally distilled under vacuum. The fraction boiling at 106-108 °C at 1 torr was collected and kept under nitrogen (lit. 167-169 °C at 25 torr).

Purification of 3-pyridylcarbinol. Reagent grade 3-pyridylcarbinol (Aldrich) was dried over magnesium sulfate for two days then fractionally distilled under vacuum. The fraction boiling at 92-94 °C at 1 torr was kept under nitrogen.

Purification of 1-undecene. Reagent grade 1-undecene from Aldrich was used without further purification.

Purification of 1-undecanol. Reagent grade 1-undecanol from Aldrich was used without further purification.

Purification of undecanoic acid. Commercial undecanoic acid was recrystallized twice from ethanol. M.p. 27-28 °C.

Purification of selenium dioxide. Selenium oxide from Aldrich was used without further purification.

Purification of lauroyl peroxide. Commercial lauroyl peroxide (Aldrich) was recrystallized twice from benzene and dried under vacuum m.p. 55-56 °C (sealed tube) (lit. 55-57 °C).

Preparation of the Compounds

Preparation of 8-chloro-5-methylquinoline. 4-Chloro-3-aminotoluene was converted to 8-chloro-5-methylquinoline by the method of Gatterman and Kaiser[131] as previously described.[99] To a mixture of 32 g of glycerol, 20 g of the sodium salt of m-nitrobenzenesulfonic acid and 18 g of 4-chloro-3-aminotoluene was added 30 g of concentrated sulfuric acid in small portions over a one hour period. The mixture was allowed to stand overnight then heated gently for one hour (after 30 minutes, a dark black color appeared). The mixture was then refluxed at 135 °C for 8 hours. The solution was diluted with 200 mL of water and treated with excess sodium nitrite (25 g). The solution was then boiled to decompose any unchanged 4-chloro-3-aminotoluene. The solution was then made alkaline with sodium hydroxide pellets and steam distilled to yield 14.2 g of 8-chloro-5-methylquinoline. The NMR spectrum showed no starting material to be present.

Preparation of 5-methylquinoline. 8-Chloro-5-methylquinoline was hydrodechlorinated by the method of Yoshikawa[133] as previously reported.[99] A solution of 5 g of 8-chloro-5-methylquinoline in 150 mL of 10% potassium hydroxide in methanol was hydrogenated over 1.5 g of 10% palladium on charcoal for 12 hours. The mixture was then filtered through celite. To the filtrate was added

300 mL of water. The resulting solution was extracted with two 100 mL portions of chloroform. The chloroform was thorougly washed with water and dried over calcium chloride. A red-brown oil was obtained. This procedure was repeated twice and a total amount of 12.2 g of material was obtained.

Purification of 5-methylquinoline. The 5-methylquinoline obtained was distilled under vacuum from barium oxide. The fraction boiling at 102 °C at 6 torr was collected and kept under argon. The purity was checked by GLC which showed 99% of a single component ^{1}H NMR $CDCl_3$ δ ppm 2.67 (s, 3H), 7.35 (m, 2H), 7.57 (m, 1H), 7.96 (d, 1H), 8.30 (d, 1H), 8.90 (dd, 1H).

Preparation of 1-chloroundecane. 1-Chloroundecane was prepared by a standard procedure.[133] To 17 mL of freshly distilled thionyl chloride was added 10 g of 1-undecanol dropwise over a 90 minute period. The mixture was then refluxed for 2 hours. The brown-yellow solution was then fractionally distilled under nitrogen. The fraction boiling at 218 °C was collected. GLC analysis showed no starting material to be present. IR spectroscopy showed no absorption in the 3300-3600 cm^{-1} range.

Preparation of 1,1,1-trichlorododecane. 1,1,1-Trichlorododecane was prepared by addition of chloroform to 1-undecene.[134] Nitrogen was bubbled through a solution of 5 g of 1-undecene in 16 mL of dried chloroform for a period of 30 minutes. To this well stirred solution was added 0.095 g of benzoyl peroxide. The solution was then refluxed for four hours. A second portion of benzoyl peroxide (0.097 g) was added and reflux was continued for nine additional hours. GLC analysis of the reaction mixture, after evaporation of solvent, showed only a single product. Negative ion mode chemical ionization analysis showed a molecular ion that corresponds to a trichlorododecane.

Preparation of 1,1,1,3-tetrachloroundecane. 1,1,1,3-Tetrachloroundecane was prepared by the method described by Kharasch et al.[134] A solution of 5.2 g of 1-undecene and 0.53 g of benzoyl peroxide in 10 mL of dried carbon tetrachloride was put in a thick wall ampoule. After a series of freeze-thaw cycles the ampoule was sealed under a nitrogen atmosphere. It was then heated to 105 °C for five hours. The ampoule was cooled and opened. GLC and MS techniques were used to characterize the complex product mixture. No isolation of 1,1,1,3-tetrachloroundecane was attempted, however, the retention time of this material could be evaluated for comparison with reaction mixtures.

Preparation of undecyl dodecanoate. This ester was made in the usual manner via the acyl chloride from the corresponding acid and alcohol.[135] It was recrystallized twice from aqueous ethanol. The overall yield was 63%.

Preparation of 5,6,7, and 8-quinolinecarboxyaldehydes. These aldehydes were prepared by the method described by Rodionov and Berkengum for the selenium oxide oxidation of the corresponding methylquinolines.[136] These aldehydes were obtained by the same method as described below for 8-quinolinecarboxyaldehyde.

A mixture of 10 g of 8-methylquinoline and 8.5 g of selenium oxide was heated to 150 °C. When the vigorous reaction started the heat source was removed. The temperature rose to 225 °C. The mixture was then heated to 250 °C to remove unreacted 8-methylquinoline by evaporation. After cooling the residue, ether was added which selectively dissolved the aldehyde but not the byproduct, carboxylic acid. The ether solution was washed with water and dried over magnesium sulfate. After the removal of the solvent, recrystallization from water gave 8.3 g of white crystals that melted at 93-93.5 °C; lit.[136] 94-95 °C. NMR analysis showed a new signal for the aldehyde proton. No signal for the methyl group in the starting molecule was observed. The results are summarized in Table 21.

Table 21. Yields and selected physical properties of 5,6,7, and 8-quinoline-carboxaldehydes.

Isomer	% yield	m.p., °C	m.p.,[a] °C	δ CHO ppm
5	40	97-98	95.5-96.5	10.23
6	67	76-77	75-76	10.21
7	85	86-87.5	85-86	10.28
8	68	93-93.5	94-95	11.46

[a] From reference 136

Preparation of 5,6,7, and 8-hydroxymethylquinoline. The 5,6,7 and 8-quinolinecarbinols were obtained by sodium borohydride reduction of the corresponding aldehydes.[137] These alcohols were prepared in good yields by the method described below for the preparation of 8-hydroxymethylquinoline.

A solution of 8-quinolinecarboxaldehyde (2 g) and sodium hydroxide (0.023 g) in methanol (30 mL) was stirred under a nitrogen atmosphere. To this mixture was added 0.1805 g of sodium borohydride in small portions over a 20 minute period. The mixture was then stirred under a nitrogen atmosphere at room temperature for eight hours. The solvent was removed under vacuum and the remaining material dissolved in 50 mL of water. This solution was then neutralized with 5% hydrochloric acid and extracted with benzene. The solid obtained was recrystallized twice from benzene-ligroin (2:1). The white granular solid obtained melted at 80-81 °C (lit.[138] 77-78 °C). NMR analysis showed no signal for the aldehyde proton and a new signal at 5.21 ppm (s, 2H). Signals for OH protons were observed in all

cases. The results for the preparation of the quinolinecarbinols are summarized in Table 22.

Table 22. Yields and selected physical properties of 5,6,7, and 8-hydroxymethylquinolines.

Isomer	% yield	m.p., °C	m.p.,[a] °C	δ CH_2OH ppm
5	58	141-143	137-138	5.15
6	75	76-76.5	79-80	4.91
7	84	58-59	59-60	4.85
8	70	80-81	77-78	5.21

[a] From reference 137

Preparation of 5,6,7, and 8-chloromethylquinoline. These compounds were synthesized from their corresponding carbinols by the method of Kaslow and Schlatter.[107] This method is illustrated using the preparation of the 8-chloromethylquinoline as an example. 8-Hydroxymethylquinoline (2.5 g) was dissolved in 80 mL of calcium hydride dried benzene. The solution was then saturated with hydrogen chloride. The white hydrochloride precipitated and was isolated by filtration. The 8-hydroxymethyquinoline hydrochloride obtained (2.9 g (94%)) was air dried in the dark. The hydrochloride salt was dissolved in 7 mL of freshly distilled thionyl chloride and refluxed for one hour. The reaction mixture was then cooled and 200 mL of dried benzene was added. A white precipitate was collected and

air dried in the dark. It was then dissolved in 30 mL of ice-water and neutralized with a chilled 1N sodium hydroxide solution. The crude white 8-chloromethylquinoline was isolated by filtration. It was then dissolved in hot ligroin (b.p. 60-85 °C) and the solution was cooled to -15 °C using dry ice-ethylene glycol bath. A yield of 1.6 g (61%) of short white needles was obtained, m.p. 54 °C (lit.[107] 53.5-54.5 °C; lit.[139] 56 °C). NMR analysis showed a new signal δ 5.35 ppm which corresponds to the protons of the CH_2Cl group. No signal corresponding to the protons of the exocyclic methylene group in the starting carbinol was observed. The data for the preparation of the 5,6,7 and 8-chloromethylquinoline isomers is found in Table 23.

Table 23. Yields and selected physical properties of 5,6,7, and 8-chloromethylquinolines.

Isomer	% yield[a]	m.p., °C	m.p.,[b] °C	δ CH_2Cl ppm
5	81.5	90-90.5	88-89.5	5.02
6	71.6	71	70.5-71	4.15
7	77.0	54-55	53-54	4.79
8	56.4	54	53.5-45.5	5.35

[a] Overall yield for the two steps

[b] From reference 107

Preparation of 4-methylquinoline N-oxide. Lepidine N-oxide was prepared in an excellent yield (92%) from lepidine by the method described by Ochiai and

Tanida.[105] Lepidine (5 g) was dissolved in 5 mL of acetic acid and immediately 11 mL of 30% aqueous solution of hydrogen peroxide was added. The solution was then heated to 90 °C for ten hours. The reaction mixture was cooled and 0.25 g of 10% palladium on carbon was added to decompose the unreacted hydrogen peroxide. After filtration, the solvent was removed under vacuum and the dark residue dissolved in 5% aqueous potassium hydroxide solution. It was then extracted with chloroform. The chloroform solution was dried over magnesium sulfate. After removal of solvent, a pale yellow solid was obtained. M.p. 120-122 °C (lit.[105] 113-115 °C; lit[140] 119-121 °C). NMR analysis showed no signals characteristic of unreacted 4-methylquinoline.

Preparation of 2-methylquinoline N-oxide. Quinaldine N-oxide was prepared from quinaldine by the same method described for lepidene N-oxide.[105] However, NMR analysis of the brownish solid showed that both product and starting material were present in 4:1 ratio.

Purification of 2-methylquinoline N-oxide. Quinaldine N-oxide, 2.5 g, was purified by flash column chromatography on silica gel, using ethyl acetate:hexane (1:4) as eluant. After the 2-methylquinoline impurity was collected the column was flushed with 10% methanol in chloroform solution. After evaporation of solvents 0.42 g of quinaldine were recovered and 1.8 g of pure 2-methylquinoline N-oxide were also obtained (74%). M.p. 76-77.5 °C (lit.[141] 77-78 °C). The results are shown in Table 24.

Table 24. Yields and selected physical properties of 2- and 4-methylquinoline N-oxides.

Isomer	% yield	m.p., °C	lit. m.p., °C	δ CH_3 ppm
2	74	76-77.5	77-78[a]	2.73
4	92	120-122	119-121[b]	2.68
			113-115[c]	

[a] From reference 141

[b] From reference 140

[c] From reference 105

Preparation of 2- and 4-chloromethylquinoline. These two compounds were prepared from the corresponding N-oxide by the method of Ochiai and Kaneko.[106] This method is described for the synthesis of 4-chloromethylquinoline.

4-Methylquinoline N-oxide (1 g) in 20 mL of calcium hydride dried N,N dimethyl formamide was treated with 3.77 g of boron trifluoride etherate and 1.45 g of tosyl chloride under a nitrogen atmosphere. This mixture was then refluxed under nitrogen for 2.5 hours. The solvent was removed under vacuum and the remaining slurry was extracted with chloroform. The chloroform layer was washed with 8% aqueous ammonium hydroxide solution then extracted with an 8% hydrochloric acid solution. The aqueous layer was made alkaline and extracted with ether. The ether was dried over magnesium sulfate. After evaporation of solvent 0.4 g of brown residue was obtained. NMR analysis showed that both starting material (23%) and product (77%) were present. The mixture was purified by flash column chromatography on alumina. Recrystallization from ligroin of the

yellow solid obtained after chromatography gave 0.32 g of white short needles. M.p. 57 °C (lit.[106] 56-57 °C). NMR analysis showed a new signal at δ 5.02 (s, 2H) and no signal corresponding to protons of starting material was observed. The data for the 2- and 4-chloromethylquinoline is summarized in Table 25.

Table 25. Yields and selected physical properties of 2- and 4-chloromethylquinolines.

Isomer	% yield	m.p., °C	lit. m.p.,[a] °C	δ CH_2Cl ppm
2	73	54-56	54-55.7	
4	40	57	56-57	5.02

[a] From reference 106

Preparation of 3-cyanoquinoline. 3-Cyanoquinoline was prepared from 3-bromoquinoline by the method described by Gilman and Spatz.[142] In a round-bottom flask set for immediate vacuum distillation were put 15.0 g of 3-bromoquinoline and 15.7 g of cuprous cyanide. It was then heated and put under vacuum immediately after the materials melted. The condenser was kept warm to avoid clogging. After the reaction was completed, the white solid was washed off the glass walls with chloroform. After evaporation of solvent and recrystallization from ethanol 9.9 g (89%) of pure 3-cyanoquinoline was obtained. M.p. 106 °C (lit.[142] 106-108 °C; lit.[143] 107 °C).

Preparation of 3-quinolinecarboxylic acid. 3-Quinolinecarboxylic acid was prepared by hydrolysis of 3-cyanoquinoline.[142] 3-Cyanoquinoline (9.9 g) and 8 g

of sodium hydroxide were dissolved in 60 mL of methanol and 30 mL of water. The mixture was refluxed for three hours. The solvent was removed *in vacuo* and the solid residue was dissolved in water and acidified with dilute hydrochloric acid solution. The white acid precipitate was isolated by filtration and recrystallized from water-acetic acid. M.p. 279-281 °C (lit.[142] 280-281 °C).

Preparation of methyl 3-quinolinecarboxylate. Methyl 3-quinoline-carboxylate was prepared by esterification of the acid with diazomethane.[144] The ester was prepared by addition of a 10% excess of a distilled ethereal solution of diazomethane to a suspension of the acid (5 g) in ether at 0 °C. The solution was allowed to warm to room temperature and stirred overnight. After evaporation of solvent and recrystallization from hexane, 5 g (92%) of white solid was obtained. M.p. 73-74 °C (lit.[144] 73.5-74.5 °C; lit.[145] 73-74 °C). NMR showed a new signal at δ 4.21 ppm (s, 3H).

Preparation of 3-hydroxymethylquinoline. The 3-hydroxymethylquinoline was obtained by sodium-bis(2-methoxyethoxy)aluminum hydride reduction of the preceding compound. A modification of this method is described by Chvalovsky et al.[146] for the reduction of ethyl nicotinate to 3-pyridylmethanol. The reaction was carried at room temperature rather than the 80 °C temperature used by the original authors.[145] In a flask kept under an inert atmosphere of nitrogen, 5.3 g of ester were dissolved in 90 mL of calcium hydride dried benzene. To this well stirred solution was added dropwise 10 mL (1.1 eq.) of 3.4 M solution of sodium-bis(2-methoxyethoxy)aluminum hydride in toluene over a period of 20 min. This mixture was stirred at room temperature overnight. A 10% hydrochloric acid solution was added to remove the inorganic salts and the phases separated. The aqueous layer was extracted with benzene. The combined organic layers were dried over magnesium sulfate. The solvent was evaporated and 5.4 g of a brown solid was obtained. It was

then recrystallized from benzene-ligroin (2:1). 3.8 g (81%) of a granular white solid was obtained. M.p. 74-76 °C (lit.[138] 71-77 °C; lit.[147] 65-67 °C). NMR analysis showed signals corresponding only to 3-quinolinecarbinol. The signal at δ 4.85 (s, 2H) was attributed to the carbinol protons.

Preparation of 3-chloromethylquinoline. 3-Chloromethylquinoline was prepared in a good yield (82%) starting from the carbinol. The method employed was that described for the preparation of 5, 6, 7 and 8-chloromethylquinoline isomers. M.p. lit.[107] 33-34 °C. NMR analysis showed no signal corresponding to protons of starting alcohol, but a new signal at δ 4.71 ppp (s, 2H).

Preparation of 3-chloromethylpyridine hydrochloride salt. This salt was prepared in 87% yield by the method of Kaslow and Schlatter[107] as previously described for the preparation of chloromethylquinolines from the corresponding carbinols.

Preparation of chloromethylpyridines. 2, 3 and 4-Chloromethylpyridines were prepared from the corresponding chloromethylpyridine hydrochloride salts. The picolyl chloride hydrochloride salt (1 g) was dissolved in 10 mL ice water and neutralized with 1 N sodium hydroxide solution. This solution was then extracted with ether. The ether solution was dried over magnesium sulfate and the solvent removed *in vacuo*. The liquid residue was then put under high vauum to remove any trace of the ether solvent. NMR analyses showed only absorption associated with the given picolyl chloride.

Determination of Relative Rates of Hydrogen Atom Abstraction by Undecyl Radical

Solutions of lauroyl peroxide, carbon tetrachloride and the chosen arylmethane were prepared in the molar ratio 1:50:50. These solutions were equally

divided into several ampoules. After a series of freeze-thaw cycles, the ampoules were sealed under a reduced pressure of nitrogen. They were then placed in a constant temperature oil bath maintained at 70 ± 1 °C for 90 hours. After completion of the reaction, the ampoules were cooled down and opened. Aliquots (0.5 mL) of the reaction mixture were diluted to 10 mL with a 9.521 10^{-4} M solution of the GLC internal standard, chlorobenzene, in acetone. These solutions were then analyzed for undecane, 1-undecene and 1-chloroundecane.

All determinations were run in replicate. The amount of undecane, 1-undecene and 1-chlorobenzene were determined using the equation below.

$$\text{moles of analyte} = \frac{\text{\% Area analyte peak}}{\text{\% Area I.S. peak}} \times F_{analyte} \times (\text{moles I.S.}) \qquad \text{eq. 100}$$

The internal standard is represented by I.S. The correction factors, $F_{analyte}$, were determined from solutions of known concentration under identical analytical conditions.

Determination of Relative Rates of Chlorine Atom Transfer

Solutions of 1-chloromethylnaphthalene, the chosen arylmethyl chloride, azo-bis-butyronitrile, internal standard (p-di-tert-butylbenzene) and deuterobenzene were prepared in approximate molar ratio 10:10:1:600. A small amount was reserved for analysis of starting amterial. To the remaining solution was added triphenyltin hydride in an approximate ratio of 1:2 to 1-chloro-methylnaphthalene. This final solution was equally divided into several ampoules. The ampoules were sealed under a reduced pressure of nitrogen after a series of freeze-thaw cycles. They were then put in a constant temperature oil bath maintained at 70 ± 1 °C for two hours. After completion of the reaction, the

ampoules were cooled and opened. The reaction mixtures were analyzed for the disappearance of the chloromethylarenes via NMR using the aliphatic protons of p-di-tert-butylbenzene as an internal standard. The amounts of the arylmethyl chlorides were determined by the equation shown below.

$$\text{moles of analyte} = \frac{\text{Area analyte peak}}{\text{Area of I.S.}} \times 9 \times (\text{moles of I.S.}) \qquad \text{eq. 101}$$

The internal standard is denoted at I.S.

The relative rates of chlorine atom transfer from the arylmethyl chlorides (QCl) vs. 1-chloromethylnaphthalene NCl) were obtained using the usual competitive procedure shown in equation 102.

$$\frac{k_{QCl}}{k_{NCl}} = \frac{\text{Log}\frac{[QCl]_i}{[QCl]_f}}{\text{Log}\frac{[NCl]_i}{[NCl]_f}} \qquad \text{eq. 102}$$

$(QCl)_i$ and $(NCl)_i$ are the initial number of moles of arylmethyl chloride and 1-chloromethylnaphthalene. $(QCl)_f$ and $(NCl)_f$ are the corresponding final number of moles present.

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APPENDIX

Table 26. Thermolysis of lauroyl peroxide in a mixture of carbon tetrachloride and toluene at 70 °C.

$\frac{[CCl_4]}{[QH]} = 0.624$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 250.173 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	8.040	8.601	10.699	0.052
1[b]	7.959	8.483	10.916	0.048
2[a]	8.122	8.682	10.581	0.053
2[b]	8.122	8.682	10.581	0.048
3[a]	8.131	8.682	10.690	0.052
3[b]	8.094	8.565	10.717	0.044
4[a]	8.049	8.574	10.672	0.048
4[b]	8.103	8.664	10.774	0.052

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.031 \pm 0.0002$

Table 27. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 1-methylnaphthalene at 70 °C.

$\frac{[CCl_4]}{[QH]} = 1.006$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 245.078 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.380	1.773	6.078	0.229
1[b]	0.353	1.736	5.915	0.234
2[a]	0.326	1.700	6.367	0.216
2[b]	0.371	1.791	6.792	0.206
3[a]	0.298	1.637	5.815	0.230
3[b]	0.317	1.718	6.430	0.218
4[a]	0.398	1.733	5.851	0.235
4[b]	0.362	1.800	6.014	0.239
5[a]	0.461	1.899	6.304	0.288
5[b]	0.434	1.944	6.539	0.231

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.228 \pm 0.0010$

Table 28. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 2-methylnaphthalene at 70 °C.

$\frac{[CCl_4]}{[QH]} = 1.002$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 348.694 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.190	6.159	43.890	0.136
1[b]	0.208	5.481	31.647	0.133
2[a]	0.226	6.258	44.029	0.137
2[b]	0.217	6.177	42.571	0.140
3[a]	0.235	6.078	43.604	0.134
3[b]	0.217	6.186	42.915	0.130
4[a]	0.181	6.231	44.815	0.135
4[b]	0.199	6.150	43.757	0.136
5[a]	0.190	6.195	43.514	0.138
5[b]	0.208	6.231	45.977	0.131

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.135 \pm 0.003$

Table 29. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 2-methylpyridine at 70 °C.

$\frac{[CCl_4]}{[QH]} = 1.020$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 455.180 µmoles

GC run	Un(-H) µmoles	UnH µmoles	UnCl µmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.326	2.536	11.558	0.191
1[b]	0.262	2.660	11.757	0.204
2[a]	0.271	3.183	11.603	0.251
2[b]	0.317	3.644	12.616	0.264
3[a]	0.235	2.671	11.296	0.220
3[b]	0.280	2.865	11.513	0.225
4[a]	0.253	3.223	12.417	0.239
4[b]	0.226	3.072	12.354	0.230
5[a]	0.298	3.096	12.634	0.229
5[b]	0.262	3.034	12.291	0.225

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.232 \pm 0.020$

Table 30. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 3-methylpyridine at 70 °C.

$\frac{[CCl_4]}{[QH]} = 1.057$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 459.570 µmoles

GC run	Un(-H) µmoles	UnH µmoles	UnCl µmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.118	0.968	27.421	0.031
1[b]	0.118	0.932	28.082	0.029
2[a]	0.109	0.959	26.598	0.032
2[b]	0.127	0.959	26.562	0.031
3[a]	0.118	0.986	27.227	0.032
3[b]	0.118	0.968	27.222	0.031
4[a]	0.127	0.941	27.227	0.030
4[b]	0.127	0.950	27.322	0.030
5[a]	0.118	0.968	27.231	0.031
5[b]	0.118	0.959	27.241	0.031

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.033 \pm 0.001$

Table 31. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 4-methylpyridine at 70 °C.

$\frac{[CCl_4]}{[QH]} = 0.988$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 458.069 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.127	6.964	19.318	0.354
1[b]	0.127	7.000	19.173	0.357
2[a]	0.127	6.910	19.526	0.350
2[b]	0.136	6.873	19.264	0.350
3[a]	0.118	6.819	19.191	0.349
3[b]	0.127	6.849	19.535	0.344
4[a]	0.109	7.036	19.390	0.357
4[b]	0.127	6.982	19.734	0.347
5[a]	0.109	6.955	19.173	0.357
5[b]	0.118	6.946	19.653	0.347

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.347 \pm 0.005$

Table 32. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 2-methylquinoline at 70 °C.

$\frac{[CCl_4]}{[QH]} = 1.001$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 480.176 µmoles

GC run	Un(-H) µmoles	UnH µmoles	UnCl µmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.212	5.769	30.201	0.184
1[b]	0.216	5.748	30.230	0.183
2[a]	0.220	5.751	30.125	0.184
2[b]	0.225	5.758	29.908	0.185
3[a]	0.221	5.763	30.451	0.186
3[b]	0.219	5.770	30.500	0.182
4[a]	0.217	5.759	30.120	0.184
4[b]	0.218	5.757	29.941	0.185
5[a]	0.221	5.763	29.796	0.186
5[b]	0.218	5.769	30.333	0.183

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.184 \pm 0.001$

Table 33. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 3-methylquinoline at 70 °C.

$\frac{[CCl_4]}{[QH]} = 0.989$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 281.710 µmoles

GC run	Un(-H) µmoles	UnH µmoles	UnCl µmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.606	2.614	23.551	0.085
1[b]	0.624	2.451	24.545	0.074
2[a]	0.633	2.532	24.690	0.077
2[b]	0.624	2.578	24.491	0.080
3[a]	0.606	2.514	22.890	0.083
3[b]	0.597	2.469	22.990	0.081
4[a]	0.615	2.550	23.415	0.083
4[b]	0.633	2.668	23.487	0.087
5[a]	0.070	2.650	23.641	0.085
5[b]	0.615	2.614	23.695	0.084

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.082 \pm 0.004$

Table 34. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 4-methylquinoline at 70 °C.

$\frac{[CCl_4]}{[QH]} = 1.026$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 215.237 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.000	7.597	16.460	0.462
1[b]	0.000	7.606	16.822	0.452
2[a]	0.000	7.633	17.193	0.444
2[b]	0.000	7.651	16.858	0.454
3[a]	0.000	7.633	17.193	0.444
3[b]	0.000	7.660	17.057	0.444
4[a]	0.000	7.669	16.659	0.460
4[b]	0.000	7.615	16.786	0.454
5[a]	0.000	7.624	17.238	0.442
5[b]	0.000	7.633	17.211	0.443

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.463 \pm 0.018$

Table 35. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 5-methylquinoline at 70 °C.

$\frac{[CCl_4]}{[QH]} = 0.998$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 278.955 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1	0.262	4.965	23.641	0.199
2	0.217	4.594	22.691	0.193
3	0.199	4.495	22.592	0.190
4	0.235	4.667	23.580	0.188

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.193 \pm 0.005$

Table 36. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 6-methylquinoline at 70 °C.

$\frac{[CCl_4]}{[QH]} = 0.993$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 269.201 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.217	1.139	10.022	0.092
1[b]	0.210	1.144	10.152	0.092
2[a]	0.224	1.149	9.439	0.098
2[b]	0.219	1.152	9.619	0.097
3[a]	0.205	1.138	9.330	0.100
3[b]	0.209	1.133	9.059	0.102
4[a]	0.253	1.152	9.667	0.093
4[b]	0.242	1.158	9.745	0.094
5[a]	0.230	1.145	9.242	0.099
5[b]	0.227	1.149	9.220	0.100

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.096 \pm 0.004$

Table 37. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 7-methylquinoline at 70 °C.

$\frac{[CCl_4]}{[QH]} = 1.026$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 140.980 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.244	1.146	1.204	0.093
1[b]	0.226	1.142	1.204	0.095
2[a]	0.235	1.139	1.172	0.095
2[b]	0.217	1.138	1.170	0.095
3[a]	0.226	1.158	1.176	0.097
3[b]	0.208	1.152	1.136	0.100
4[a]	0.199	1.138	1.141	0.098
4[b]	0.199	1.133	1.150	0.100
5[a]	0.226	1.149	1.155	0.097
5[b]	0.244	1.148	1.169	0.096

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.096 \pm 0.002$

Table 38. Thermolysis of lauroyl peroxide in an equimolar mixture of carbon tetrachloride and 8-methylquinoline at 70 °C.

$\frac{[CCl_4]}{[QH]} = 1.003$ Conditions: 70 ± 1 °C; 90 hours

Lauroyl peroxide: 467.10 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.371	1.537	35.055	0.033
1[b]	0.389	1.673	34.847	0.037
2[a]	0.461	1.655	34.286	0.035
2[b]	0.452	1.691	35.751	0.035
3[a]	0.425	1.592	34.837	0.033
3[b]	0.443	1.709	35.751	0.035
4[a]	0.479	1.610	37.008	0.031
4[b]	0.470	1.773	34.548	0.038
5[a]	0.416	1.700	34.241	0.038
5[b]	0.425	1.673	34.548	0.036

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.035 \pm 0.002$

Table 39. Thermolysis of lauroyl peroxide in an equimolar mixture of quinoline and carbon tetrachloride at 70 °C for 43 hours.

$\frac{[CCl_4]}{[QH]} = 1.008$ Conditions: 70 ± 1 °C; 43 hours

Lauroyl peroxide: 245.560 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.367	1.095	5.136	0.142
1[b]	0.203	0.998	5.650	0.141
2[a]	0.167	0.414	5.019	0.149
2[b]	0.235	0.478	4.871	0.151

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.148 \pm 0.006$

Table 40. Thermolysis of lauroyl peroxide in an equimolar mixture of quinoline and carbon tetrachloride at 70 °C for 57 hours.

$\frac{[CCl_4]}{[QH]} = 1.008$ Conditions: 70 ± 1 °C; 57 hours

Lauroyl peroxide: 245.560 µmoles

GC run	Un(-H) µmoles	UnH µmoles	UnCl µmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.596	1.864	6.309	0.201
1[b]	0.607	1.794	6.027	0.197
2[a]	0.621	1.776	6.111	0.189
2[b]	0.617	1.827	0.271	0.193

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.195 \pm 0.005$

Table 41. Thermolysis of lauroyl peroxide in an equimolar mixture of quinoline and carbon tetrachloride at 70 °C for 73 hours.

$\frac{[CCl_4]}{[QH]} = 1.008$ Conditions: 70 ± 1 °C; 73 hours

Lauroyl peroxide: 245.560 μmoles

GC run	Un(-H) μmoles	UnH μmoles	UnCl μmoles	$\frac{UnH - Un(-H)}{UnCl}$
1[a]	0.734	2.711	7.819	0.253
1[b]	0.785	2.647	7.542	0.247
2[a]	0.753	2.562	7.391	0.245
2[b]	0.708	2.517	7.210	0.251

Average $\frac{UnH - Un(-H)}{UnCl} \cdot \frac{[CCl_4]}{[QH]} = 0.250 \pm 0.004$

Table 42. Relative rates of disappearance of 2-chloromethylpyridine vs. 1-chloromethylnaphthalene.

AIBN: 60.976 µmoles
Ph_3SnH: 310.711 µmoles
P-di-tert-butylbenzene: 49.913 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	2-chloromethylpyridine	434.393	300.077	134.316	30.9	0.429
	1-chloromethylnaphthalene	486.053	204.843	281.210	57.9	
2	2-chloromethylpyridine	434.393	336.464	97.929	22.5	0.392
	1-chloromethylnaphthalene	486.053	253.358	232.695	47.9	
3	2-chloromethylpyridine	434.393	302.772	131.621	30.3	0.454
	1-chloromethylnaphthalene	486.053	219.218	266.835	54.9	
4	2-chloromethylpyridine	434.393	334.549	89.844	20.7	0.407
	1-chloromethylnaphthalene	486.053	274.472	211.581	43.5	

Average k_{rel} = 0.421 ± 0.027

Table 43. Relative rate of disappearance of 3-chloromethylpyridine vs. 1-chloromethylnaphthalene.

AIBN: 59.146 µmoles
Ph_3SnH: 285.456 µmoles
P-di-tert-butylbenzene: 245.078 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	3-chloromethylpyridine	374.978	330.718	77.866	20.8	0.320
	1-chloromethylnaphthalene	582.138	391.878	190.260	32.7	
2	3-chloromethylpyridine	374.978	297.112	110.035	41.5	0.345
	1-chloromethylnaphthalene	582.138	297.112	285.844	49.1	
3	3-chloromethylpyridine	374.978	323.956	51.022	15.7	0.321
	1-chloromethylnaphthalene	582.138	370.480	211.658	36.4	
4	3-chloromethylpyridine	374.978	299.982	74.996	24.0	0.373
	1-chloromethylnaphthalene	582.138	319.653	262.485	45.1	

Average k_{rel} = 0.340 ± 0.025

Table 44. Relative rate of disappearance of 4-chloromethylpyridine vs. 1-chloromethylnaphthalene.

AIBN: 66.463 µmoles
Ph_3SnH: 302.260 µmoles
P-di-tert-butylbenzene: 52.540 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	4-chloromethylpyridine	452.527	367.264	85.263	18.8	0.440
	1-chloromethylnaphthalene	463.403	287.972	175.431	37.9	
2	4-chloromethylpyridine	452.527	361.265	91.262	20.2	0.464
	1-chloromethylnaphthalene	463.403	285.135	178.268	38.5	
3	4-chloromethylpyridine	452.527	380.179	72.348	16.0	0.409
	1-chloromethylnaphthalene	463.403	301.685	161.718	34.9	
4	4-chloromethylpyridine	452.527	373.087	79.440	17.6	0.425
	1-chloromethylnaphthalene	463.403	294.119	169.284	36.5	

Average k_{rel} = 0.435 ± 0.023

Table 45. Relative rate of disappearance of 2-chloromethylquinoline vs. 1-chloromethylquinoline.

AIBN: 73.171 µmoles
Ph_3SnH: 424.480 µmoles
p-di-tert-butylbenzene: 91.946 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	2-chloromethylquinoline	456.54	201.913	254.627	45.3	1.135
	1-chloromethylquinoline	562.13	273.907	288.223	51.3	
2	2-chloromethylquinoline	456.54	209.361	247.179	44.0	1.057
	1-chloromethylquinoline	562.13	270.597	291.533	51.9	
3	2-chloromethylquinoline	456.54	239.152	217.388	38.7	0.923
	1-chloromethylquinoline	562.13	284.685	277.465	49.4	
4	2-chloromethylquinoline	456.54	206.051	250.489	44.6	1.134
	1-chloromethylquinoline	562.13	278.872	283.258	50.4	

Average k_{rel} = 1.062 ± 0.100

Table 46. Relative rate of disappearance of 3-chloromethylquinoline vs. 1-chloromethylnaphthalene.

AIBN: 49.390 µmoles
Ph_3SnH: 283.450 µmoles
p-di-tert-butylbenzene 285.45 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	3-chloromethylquinoline	334.974	290.762	44.212	13.2	0.859
	1-chloromethylnaphthalene	341.670	332.373	59.397	15.1	
2	3-chloromethylquinoline	334.974	263.194	71.780	21.4	0.905
	1-chloromethylnaphthalene	341.670	300.124	91.546	23.4	
3	3-chloromethylquinoline	334.974	269.956	65.018	19.4	0.887
	1-chloromethylnaphthalene	341.670	306.886	84.784	21.6	
4	3-chloromethylquinoline	334.974	294.931	39.043	11.7	0.897
	1-chloromethylnaphthalene	341.670	341.216	50.454	12.9	

Average k_{rel} = 0.887 ± 0.020

Table 47. Relative rate of disappearance of 4-chloromethylquinoline vs. 1-chloromethylnaphthalene.

AIBN: 59.146 µmoles
Ph_3SnH: 285.456 µmoles
P-di-tert-butylbenzene: 245.078 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	4-chloromethylquinoline	380.061	219.278	160.772	42.3	1.532
	1-chloromethylnaphthalene	459.265	320.954	138.311	30.1	
2	4-chloromethylquinoline	380.061	229.928	150.133	39.5	1.639
	1-chloromethylnaphthalene	459.265	338.095	121.170	26.4	
3	4-chloromethylquinoline	380.061	238.974	141.267	37.2	1.566
	1-chloromethylnaphthalene	459.265	341.050	118.215	25.7	
4	4-chloromethylquinoline	380.061	248.252	131.809	34.7	1.568
	1-chloromethylnaphthalene	459.265	349.916	109.349	23.8	
5	4-chloromethylquinoline	380.061	252.980	127.081	33.4	1.406
	1-chloromethylnaphthalene	459.265	344.006	115.259	25.1	

Average k_{rel} = 1.544 ± 0.082

Table 48. Relative rate of disappearance of 5-chloromethylquinoline vs. 1-chloromethylnaphthalene.

AIBN: 56.326 µmoles
Ph_3SnH: 372.802 µmoles
p-di-tert-butylbenzene: 50.260 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	5-chloromethylquinoline	365.502	288.585	76.917	21.0	1.016
	1-chloromethylnaphthalene	340.874	270.147	70.732	20.7	
2	5-chloromethylquinoline	365.502	278.875	86.627	23.7	1.068
	1-chloromethylnaphthalene	340.879	264.606	76.273	22.4	
3	5-chloromethylquinoline	365.502	267.804	97.648	26.7	1.072
	1-chloromethylnaphthalene	340.874	255.036	85.843	25.2	
4	5-chloromethylquinoline	365.502	285.621	74.881	21.9	1.020
	1-chloromethylnaphthalene	340.879	267.670	73.209	21.5	

Average k_{rel} = 1.044 ± 0.030

Table 49. Relative rate of disappearance of 6-chloromethylquinoline vs. 1-chloromethylnaphthalene.

AIBN: 45.732 µmoles
Ph_3SnH: 305.396 µmoles
P-di-tert-butylbenzene: 58.845 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	6-chloromethylquinoline	427.921	394.556	33.365	7.8	0.636
	1-chloromethylnaphthalene	464.464	409.385	55.079	11.9	
2	6-chloromethylquinoline	427.921	386.082	41.839	9.8	0.662
	1-chloromethylnaphthalene	464.464	397.204	67.260	14.5	
3	6-chloromethylquinoline	427.921	358.543	69.378	16.2	0.656
	1-chloromethylnaphthalene	464.464	377.608	86.856	18.7	
4	6-chloromethylquinoline	427.921	342.125	85.796	20.0	0.608
	1-chloromethylnaphthalene	464.464	352.187	112.277	24.2	

Average k_{rel} = 0.641 ± 0.024

Table 50. Relative rate of disappearance of 7-chloromethylquinoline vs. 1-chloromethylnaphthalene.

AIBN: 64.024 µmoles
Ph_3SnH: 301.982 µmoles
p-di-tert-butylbenzene 66.201 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	7-chloromethylquinoline	375.955	255.006	120.949	32.2	0.982
	1-chloromethylnaphthalene	464.135	312.800	151.335	32.6	
2	7-chloromethylquinoline	375.955	252.027	123.928	33.0	0.956
	1-chloromethylnaphthalene	464.135	305.054	159.081	34.3	
3	7-chloromethylquinoline	375.955	256.198	119.757	31.9	0.965
	1-chloromethylnaphthalene	464.135	312.204	151.931	32.7	
4	7-chloromethylquinoline	375.955	255.006	120.949	32.2	0.982
	1-chloromethylnaphthalene	464.135	313.396	150.739	32.5	

Average k_{rel} = 0.971 ± 0.013

Table 51. Relative rate of disappearance of 8-chloromethylquinoline vs. 1-chloromethylnaphthalene.

AIBN: 59.146 µmoles
Ph_3SnH: 304.260 µmoles
p-di-tert-butylbenzene: 65.675 µmoles

Conditions: 70 ± 1 °C; 2 hours

Run #	Compound	µmoles Initial	µmoles Final	µmoles Used	% Rxn	k_{rel}
1	4-chloromethylquinoline	618.10	456.046	162.054	26.2	0.764
	1-chloromethylnaphthalene	618.74	413.908	204.832	66.9	
2	4-chloromethylquinoline	618.10	418.839	199.261	32.2	0.766
	1-chloromethylnaphthalene	618.74	382.080	236.660	61.8	
3	4-chloromethylquinoline	618.10	403.224	214.876	34.8	0.742
	1-chloromethylnaphthalene	618.74	363.850	254.890	58.8	
4	4-chloromethylquinoline	618.10	410.023	208.077	33.7	0.744
	1-chloromethylnaphthalene	618.74	369.827	248.913	54.8	
5	4-chloromethylquinoline	618.10	439.086	179.014	29.0	0.759
	1-chloromethylnaphthalene	618.74	399.787	218.953	64.6	

Average k_{rel} = 0.761 ± 0.012