substituent effects clearly argue in favor of a polar or dipolar transition state. It is difficult to envision how contribution of a dipolar form with presumably increased ring carbon–nitrogen bond strength could lower the activation energy to the extent observed in this study. Although no experimental data or calculations are available, it might be argued that the hydridization and ring carbon–nitrogen bonding changes required on going from starting material to transition state in an inversion mechanism could become energetically more difficult as contributions from a dipolar structure increased. All of the present data are in accord with an internal rotation mechanism in which contribution from dipolar resonance structures has reduced the nitrogen–nitrogen double bond strength and consequently the torsional barrier to rotation. Perhaps the one major argument in opposition to the internal rotation mechanism for **1–11** is the fact that similarly substituted stilbenes do not undergo facile thermal isomerization.[35]

Information regarding the mechanism of the photochemical isomerization of these dyes has proved somewhat elusive. We have been unable to detect any transient absorbance changes other than those associated with cis–trans isomerization following flash excitation. Experiments with most "triplet sensitizers" give inconclusive results since singlet sensitization[36] cannot be excluded and since quantum yields could not be measured. However, we find that etioporphyrin I, $E_T \sim 40$ kcal/mol,[37] does sensitize trans to cis isomerization of **1**. Etioporphyrin I can be excited by red light $\lambda > 600$ nm, which excludes any possibility of direct excitation of **1**. Normal singlet energy transfer is excluded by energy considerations and **1** does not quench etioporphyrin I fluorescence. Although we have found that nitrostilbenes quench metalloporphyrin triplet states and undergo cis to trans isomerization from an exciplex,[37] trans to cis isomerization from the exciplex is usually unimportant. Consequently we conclude that the observed results indicate triplet energy transfer from etioporphyrin I to **1** and subsequent isomerization *via* a low-lying triplet of **1**. Whether this is the only path for photoisomerization of **1** remains uncertain.

Acknowledgment. We are grateful to Professor E. Fischer for helpful discussion and suggestions. Support for the portion of this work carried out at the University of North Carolina, in part from the Research Corporation, in part from the National Institutes of Health (Grant No. GM 15,238), in part from the U. S. Army Research Office, Durham (Grant DA-ARO-D-31-124-G1097), and in part from the University of North Carolina Materials Research Center in conjunction with the Advanced Projects Agency (Contract SD-100), is gratefully acknowledged.

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[34] Compound **9** also shows no solvent effect and compounds 7 and **8** show only a slight solvent effect; probably these compounds also isomerize by an inversion mechanism.

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[36] A. B. Smith, III, and W. C. Agosta, *Chem. Commun.*, 466 (1970).

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Hydrogen Abstractions from Arylmethanes[1]

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Abstract: The relative rates of hydrogen abstraction from a series of 13 arylmethanes by the trichloromethyl radical were determined at 70°. An excellent correlation, with a coefficient of 0.977, was obtained when the data were correlated with the change in π-binding energies between the incipient radicals and the arylmethanes, if the π-binding energies were calculated by the SCF approach. When the data were correlated with the change in π-binding energies as calculated by the HMO approach, the correlation was poor with the coefficient of 0.855. A possible explanation for this difference might be the Hückel method's complete neglect of electron interactions. The kinetic data were also plotted against various ground-state properties such as free valence, atom–atom self-polarizability, and $\Sigma 1/r_{ij}$. In all cases only very poor correlations were obtained. The relative rates of hydrogen abstraction from a series of nine arylmethanes by the *tert*-butoxy radical were also determined at 70°. A satisfactory correlation was obtained with none of the above quantities. It is felt that the transition state for hydrogen abstraction by the trichloromethyl radical must strongly resemble the intermediate free radical. That for abstraction by the *tert*-butoxy radical probably has a structure between the ground state and the intermediate.

We have reported in an earlier communication that delocalization effects are important in the abstraction of hydrogen atoms from a series of arylmethanes by the trichloromethyl radical.[3] We would now like to discuss more fully correlations obtained in the above systems and to augment the study further with a discussion of the hydrogen abstraction reaction by the more reactive *tert*-butoxy radical.

In the past decade, attempts to correlate the rates of formation of arylmethyl carbonium ions[4,5] and car-

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[1] Taken from the Ph.D. Thesis of J. D. Unruh.

[2] (a) NSF Trainee, 1966–1970; (b) Alfred P. Sloan Fellow, 1969–1971.

[3] J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **91**, 6211 (1969).

[4] M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); 2946, 2952 (1957).

banions[6] with MO calculations have met with success. However, when these kinetic data were correlated with HMO calculations or Dewar's PMO calculations,[4] dual correlations were obtained. Compounds with an α-methylnaphthalene-like structure fell on one line and compounds with a β-methylnaphthalene-like structure fell on the other. The former compounds appeared to be less reactive than predicted relative to their β-methylnaphthalene counterparts. These dual correlations have been attributed to nonbonded interactions between a peri hydrogen and one of the hydrogens of the exocyclic methylene group in the α-methylnaphthyl type of intermediates.[4,6] Although an attractive explanation, such nonbonded interactions are suspect. Self-consistent field calculations do not show a similar trend. Dewar and Thompson found single correlations when treating the formation of both arylmethyl carbonium ions and carbanions.[7] Gleicher has also shown by strain energy calculations that the nonbonded interactions are not as severe as Hückel results would predict.[8] The dichotomy in results between the two types of calculations probably arises from the Hückel method's inherent neglect of electron interactions. As long as only alternant hydrocarbons are considered there is little difference between the two methods because the electronic field of the π system is uniform. However, in the corresponding ions the field is no longer uniform, and, as a result, the Hückel method is quite inadequate.

In view of the above results, we thought a study of the formation of the corresponding arylmethyl radicals would be of interest. In order to correlate the rates of formation of the radicals with the differences in π-bonding energies between the intermediate arylmethyl radicals and the arylmethane reactants, the Hammond postulate[9] suggests that the transition states should resemble the arylmethyl radicals. To form these radicals the trichloromethyl radical, generated from bromotrichloromethane, was chosen as the hydrogen abstracting agent. Huyser has shown that abstraction of benzylic hydrogens by this radical is endothermic with a considerable amount of bond breaking in the transition state.[10] To complement the above study, hydrogen abstraction from the same series of compounds by the *tert*-butoxy radical generated from *tert*-butyl hypochlorite was also undertaken. Walling and Jacknow have shown that this radical is quite reactive.[11] Hydrogen abstraction by *tert*-butoxy radical will be exothermic compared to hydrogen abstraction by the trichloromethyl radical.

Results and Discussion

Kinetic Studies Using Trichloromethyl Radical. The reaction sequence for hydrogen abstraction by the trichloromethyl radical is shown in eq 1–4.

$$(C_6H_5CO_2)_2 \xrightarrow{\Delta} 2C_6H_5\cdot + 2CO_2 \tag{1}$$

$$C_6H_5\cdot + BrCCl_3 \longrightarrow C_6H_5Br + \cdot CCl_3 \tag{2}$$

$$ArCH_3 + \cdot CCl_3 \xrightarrow{\text{rds}} ArCH_2\cdot + HCCl_3 \tag{3}$$

$$ArCH_2\cdot + BrCCl_3 \longrightarrow ArCH_2Br + \cdot CCl_3 \tag{4}$$

The hydrogen abstraction reactions were run in replicate relative to 1-methylnaphthalene. Reactions were carried out in sealed ampoules under a reduced pressure of nitrogen at 70.0 ± 0.1°. The solvent was a benzene–bromotrichloromethane mixture, and the initiator was benzoyl peroxide. Solutions of the two arylmethanes, benzoyl peroxide, *o*-dichlorobenzene, bromotrichloromethane, and benzene were prepared in the approximate molar ratio of 0.5:0.5:0.1:1.0:10:15. Small portions of the solutions were reserved for analysis as starting material. The remainders were then divided among the ampoules which were degassed and sealed. Reaction time varied from 5 to 40 hr. The corresponding extents of reaction led to from 10 to >90% of the hydrocarbons being consumed. Analyses by glc allowed the amounts of reactants to be determined for both before and after the reaction. From these, relative rates of disappearance could be obtained. Reasonably good agreement between amounts of hydrocarbons and bromotrichloromethane consumed was found. The relative rates of disappearance are presented in Table I.

Unfortunately these rates of disappearance need not coincide with the relative rates of hydrogen abstraction. Ring substitution in arenes by trichloromethyl radical is a well-known reaction which has been shown to occur under analogous conditions.[12] Ideally, a complete product analysis should be carried out for each arylmethane. This already arduous task is, however, made even more difficult by the high reactivity of the arylmethyl bromide products. As a means of evaluating the importance of ring substitution by the trichloromethyl radical, therefore, the following approach was adopted. Competitive reactions were run between each arylmethane and the corresponding unsubstituted parent arene. It was assumed that these pairs of compounds would show approximately the same tendency to undergo ring reaction.[13] This would equate any rate enhancement found for the arylmethane as being due to reaction at the exocyclic position. A statistical factor was introduced to correct for the possibility that an active position in the aromatic nucleus might be blocked by a methyl group.[12,14] The relative rates of reaction between arylmethanes and parent arenes are given in Table I. In general, abstraction from the methyl position accounted for between 65 and 100% of the reaction of any arylmethane. A detailed product study on 1-methylnaphthalene yields results in good agreement with those obtained *via* this competitive technique.

The changes in π-binding energies between the arylmethyl radicals and the arylmethane reactants were determined both by the simple HMO approach[16] and an SCF–LCAO–MO approach.[17] In the latter,

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[5] P. J. C. Fierens and H. Hannert, *Helv. Chim. Acta*, **38**, 2009 (1955); *Tetrahedron*, **1**, 129 (1957).

[6] A. Streitwieser and W. C. Longworthy, *J. Amer. Chem. Soc.*, **85**, 1757, 1761 (1963).

[7] M. J. S. Dewar and C. C. Thompson, *ibid.*, **87**, 4414 (1965).

[8] G. J. Gleicher, *ibid.*, **90**, 3397 (1968).

[9] G. S. Hammond, *ibid.*, **77**, 334 (1955).

[10] E. S. Huyser, *ibid.*, **82**, 394 (1960).

[11] C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

[12] E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

[13] The reaction of 9-substituted anthracenes with 2-cyano-2-propyl radicals in the meso position appears to occur at comparable rates irrespective of the nature of the substituent.[14] This system, of those studied, should be most susceptible to methyl substituent effects.[15]

[14] E. Farenhorst and E. C. Kooyman, *Nature (London)*, **175**, 598 (1955).

[15] C. A. Coulson, *J. Chim. Phys.*, **45**, 243 (1948).

[16] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

Table I. Uncorrected Rates of Disappearance of Arylmethanes Relative to Selected Substrates with the Trichloromethyl Radical at 70°

Compd X	k_X/k(1-methylnaphthalene)	k_X/k(unmethylated parent arene)
Toluene	0.162 ± 0.007	∞
1-Methyltriphenylene	0.403 ± 0.030	5.41 ± 0.72
2-Methyltriphenylene	0.539 ± 0.019	3.23 ± 0.24
3-Methylphenanthrene	0.509 ± 0.025	7.63 ± 0.76
1-Methylphenanthrene	0.663 ± 0.041[a]	3.27 ± 0.15
2-Methylnaphthalene	0.940 ± 0.078	3.17 ± 0.14
9-Methylphenanthrene	0.752 ± 0.050	5.53 ± 0.25
1-Methylnaphthalene	1.00	13.1 ± 0.6
6-Methylchrysene	2.68 ± 0.05	2.18 ± 0.17
2-Methylanthracene	6.94 ± 0.59	3.92 ± 0.52
1-Methylanthracene	22.8 ± 2.4	2.19 ± 0.14
1-Methylpyrene	23.0 ± 1.2	3.19 ± 0.24
9-Methylanthracene	122 ± 5[b]	3.68 ± 0.17

[a] Measured relative to toluene and corrected. [b] Measured relative to 1-methylpyrene and corrected.

Table II. Relative Rates of Hydrogen Abstraction from a Series of Unsubstituted Arylmethanes by Trichloromethyl Radical at 70°

Arylmethane	% methyl hydrogen abstraction	(k_X/k_0) H abstr[a]	$(\Delta E_{\pi X} - \Delta E_{\pi tol})$[b] HMO	$(\Delta E_{\pi X} - \Delta E_{\pi tol})$[b] SCF
Toluene	100	0.172 ± 0.008	(0.000)	(0.000)
1-Methyltriphenylene	84.6	0.362 ± 0.027	0.062[c]	0.076[c]
2-Methyltriphenylene	69.1	0.395 ± 0.014	0.024[c]	0.068[c]
3-Methylphenanthrene	86.9	0.547 ± 0.027	0.033	0.060
1-Methylphenanthrene	69.5	0.569 ± 0.035	0.082	0.139
2-Methylnaphthalene	68.4	0.682 ± 0.057	0.023	0.076
9-Methylphenanthrene	91.0	0.845 ± 0.056	0.092	0.178
1-Methylnaphthalene	94.3	(1.00)	0.091	0.175
6-Methylchrysene	77.0	2.19 ± 0.04	0.117	0.214
2-Methylanthracene	74.5	5.89 ± 0.47	0.048	0.215
1-Methylanthracene	54.3	13.1 ± 1.4	0.113	0.340
1-Methylpyrene	76.5	18.7 ± 1.0	0.147	0.352
9-Methylanthracene	86.4	112.0 ± 5	0.206	0.519

[a] 1-Methylnaphthalene is the reference compound. [b] In electron volts. [c] "Long bonds" set equal to 1.48 Å.

the suggestion of Pople and Nesbit was followed in maintaining separate orbitals for electrons of opposing spin in systems without a closed shell configuration.[18] The resonance integral, which was determined by a closed shell thermocycle suggested by Dewar,[17] was based on a constant carbon–carbon bond length of 1.40 Å. Self-consistency for the arylmethyl radicals was normally reached after ten iterations using SCF open shell calculations. An attempt was also made to determine the π-binding energies of the arylmethyl radicals by using open shell calculations with variable bond lengths.[17c] Unfortunately, the numerical results converged very slowly so that computer costs made this approach prohibitive. One departure from the use of constant bond lengths was, however, allowed. Calculations have suggested that there is considerable lengthening of bonds in the central ring of triphenylene.[19] These "long bonds" were given a value of 1.48 Å in the calculations of the π-binding energies of the methyltriphenylenes and their radicals.

The π-binding energies of the arylmethanes were taken as essentially those of the parent arenes. The effect of the methyl group was taken into account by using a simple inductive model which modifies the valence state ionization potentials of the carbon atoms to which the methyl groups are attached.[20]

The results of the kinetic studies and the π-binding energy calculations are summarized in Table II. The kinetics show a spread of three powers of ten. The rates are also quite dependent upon the position of the methyl group as can best be observed by examining the three methylanthracenes which have a rate spread of about 20.

The logs of the relative rates of hydrogen abstraction were plotted against the relative changes in π-binding energy. The results using the Hückel approach are shown in Figure 1. The solid line represents a correlation of all the compounds, and has a correlation coefficient of only 0.855. When the data are divided into two sets consisting of α-methylnaphthyl-type compounds and β-methylnaphthyl-type compounds, the familiar dual correlation discussed earlier is obtained. The correlation coefficients of 0.948 and 0.904, respectively, show considerable improvement over the single correlation. These correlations are still, however, rather poor.

Figure 2 shows the results of plotting the logs of the relative rates of hydrogen abstraction against the change in π-binding energy as calculated by the self-consistent field method. The solid line again represents a correlation of all the compounds. The coefficient of 0.977 indicates that the correlation is excellent. In fact, it is better than any correlations reported for the corresponding ionic systems.[8]

The tremendous improvement obtained when the data are correlated by SCF calculations rather than HMO calculations may, at first, seem surprising since the arylmethyl radicals are alternant hydrocarbons. However, in odd alternant hydrocarbons, any odd electron will interact differently with the other electrons depending upon whether they are of the same or opposite spin.[21] The resulting phenomenon of spin polarization is ignored in the HMO studies while implicitly included in the open shell SCF approach. Spin polarization has been experimentally verified in esr studies of certain conjugated radicals.[22] It would

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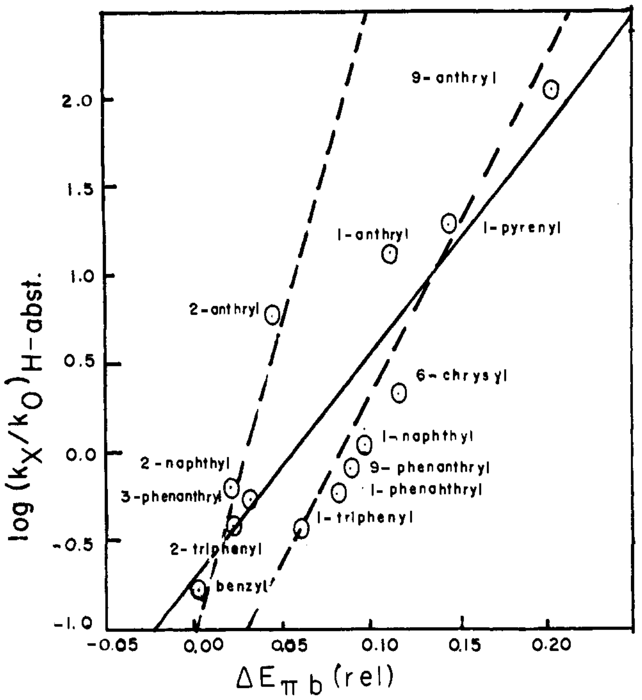

Figure 1. Relative rates of hydrogen abstraction from a series of arylmethanes by the trichloromethyl radical at 70° correlated with HMO calculations. Solid line represents a correlation based upon all compounds. Dashed lines represent separate correlations for α and β compounds.

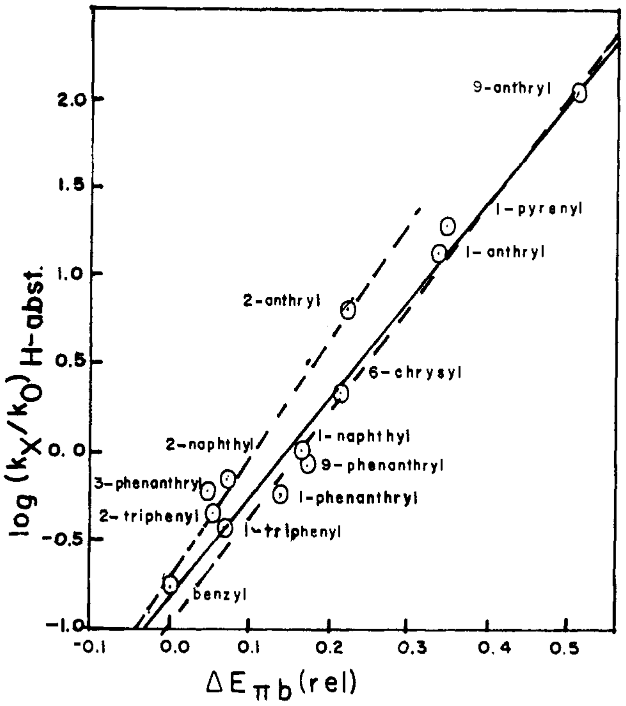

Figure 2. Relative rates of hydrogen abstraction from a series of arylmethanes by the trichloromethyl radical at 70° correlated with SCF calculations. Solid line represents a correlation based upon all compounds. Dashed lines represent separate correlations for α and β compounds.

seem that the inadequacy of the HMO correlations might be thusly explained.

Figure 2 also shows that there is a slight improvement with the SCF calculations when the dual correlation is applied. The correlation coefficients are 0.993 and 0.991 for the α-methylnaphthyl-type compounds and β-methylnaphthyl-type compounds, respectively. This may reflect a transition state of slightly higher energy for the α-methylnaphthyl-type intermediates due to nonbonded interactions. However, the change is small and it is difficult to determine whether this small improvement is real or an artifact of the calculations.

Inclusion of nonbonded interactions in the open-shell SCF calculations did not improve the correlation with these relative rates of hydrogen abstraction. A possible explanation can be given. The one-electron resonance integral used to calculate the π-binding energies of the radicals had the value determined for the closed shell calculations.[17] It has been suggested that the value of the resonance integral for open shell calculations will not be the same as for closed shell calculations.[23] As long as only the relative differences in π-binding energies are considered, the numerical value of this term is of secondary importance. However, when nonbonded interactions are included, a value of the resonance integral which allows the calculation of the absolute π-binding energies is definitely required. This problem cannot be resolved until a value of the open shell resonance integral is found.

Dewar and coworkers have suggested that closed-shell SCF calculations could be used to calculate the π-binding energies of radicals if the odd electron was replaced by two hypothetical half-electrons of opposing spin.[23] This should circumvent the problem of finding new parameters for open shell calculations. This approach did not work well, however, in the present case.

In its reaction with substituted toluenes, the trichloromethyl radical shows a correlation with the σ^+ parameters.[10] This indicates a high degree of carbonium ion character associated with the transition state for hydrogen abstraction. It has been stated that, in view of this, a correlation of the present data with the SCF calculated π energy differences between arylmethyl carbonium ions and parent arenes might be useful.[24] When all the data were treated in a single correlation, a coefficient of only 0.837 was obtained. When a distinction between α-methylnaphthyl and β-methylnaphthyl is made the respective correlation coefficients are 0.923 and 0.630! These generally poor correlations confirm what might have been the original expectation that a radical model should best fit the data. In other studies, the degree of carbonium ion character associated with the transition state for hydrogen abstraction from tertiary positions has been estimated as less than 20%.[25] It must also be pointed out that the same correlations would be obtained if the present kinetic data were plotted against a carbanion model. The rules associated with alternant hydrocarbons would decree the same relative energy changes for closed shell odd alternant system. Examples of this can readily be seen.[7]

The excellent correlations obtained when these reactions are correlated with the change in π-binding

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energy calculated by the SCF open shell method indicate that the transition state resembles the arylmethyl radicals. It would be interesting to see if correlations with ground-state properties will further substantiate this conclusion. Unfortunately, the interpretation of negative evidence is a moot point. Attempted correlations with atom–atom self-polarizabilities and free valances yielded poor correlations with the respective coefficients of 0.759 and 0.828. Correlation with quantities related to the parameter $\Sigma 1/r_{ij}$ developed by Streitwieser and Lawler was also very poor.[26] This parameter has been used with moderate success as a measure of the inductive, *i.e.*, nonconjugative, effect of aryl groups.[26,27] All of these findings would tend to depreciate the possible role played by ground-state factors in this reaction. Admittedly, however, other untried parameters might improve the results.

Attempts were also made to improve the correlations by use of a four-parameter equation which included both the changes in π-binding energies determined by the open shell SCF method, and various ground-state parameters. The correlations were slightly improved with respect to those obtained with the changes in π binding alone. However, in no case did the slope of the correlation line change by more than 15%. This would also indicate that the ground-state properties have almost negligible effects on the rate of hydrogen abstraction by the trichloromethyl radical.

Kinetic Studies using *tert*-Butoxy Radical. The hydrogen abstraction reactions were run in replicate relative to 1-methylnaphthalene in a benzene solvent at 70.0 ± 0.1° under essentially the same conditions used in the trichloromethyl radical studies. Trichloroethylene was present to trap any free chlorine formed during the reaction.[28] Solutions of the two arylmethanes, *o*-dichlorobenzene, trichloroethylene, benzoyl peroxide, *tert*-butyl hypochlorite, and benzene were prepared in the approximate molar ratios of 1.0:1.0:1.0:1.3:0.05:2.5:40. Small amounts were reserved for analysis as starting material. The remainders were placed in ampoules, degassed, and sealed. The reaction sequence is shown in eq 5–8.

$$(C_6H_5CO_2)_2 \xrightarrow{\Delta} 2C_6H_5\cdot + 2CO_2 \tag{5}$$

$$tert\text{-BuOCl} + C_6H_5\cdot \longrightarrow tert\text{-BuO}\cdot + C_6H_5Cl \tag{6}$$

$$tert\text{-BuO}\cdot + ArCH_3 \xrightarrow{\text{rds}} ArCH_2\cdot + tert\text{-BuOH} \tag{7}$$

$$ArCH_2\cdot + tert\text{-BuOCl} \longrightarrow ArCH_2Cl + tert\text{-BuO}\cdot \tag{8}$$

The reaction times were approximately 3 hr. The extent of reaction varied from 25 to 80%.

The arylmethanes were also treated in competition with their parent arenes to observe if ring substitution was occurring. Within experimental error, no reaction took place in the rings of arylmethanes derived from benzene, naphthalene, phenanthrene, triphenylene, or chrysene. However, in the case of 1-methylpyrene and the methylanthracenes, addition of *tert*-butyl hypochlorite caused immediate precipitation at room temperature. This continued until substantially all the arylmethane had been consumed. In the case of 9-methylanthracene, the product was shown to be 10-chloro-9-methylanthracene. It was assumed that ring substitution was also occurring in the other specified methylarenes. Induced decomposition of the *tert*-butyl hypochlorite may take place in the presence of these two reactive ring systems. This would not be surprising since Walling has observed induced decomposition of *tert*-butyl hypochlorite in the presence of styrene. These two compounds react spontaneously in the dark of 0° to form the one to one adduct.[29] Kooyman has shown that the relative reactivity for aromatic hydrocarbons with respect to radical substitution is: benzene < phenanthrene < triphenylene < naphthalene < chrysene ≪ pyrene ≪ anthracene.[12] A similar order holds for electrophilic substitution in aromatic systems.[7] The aromatic hydrocarbons less reactive than pyrene are apparently not reactive enough to induce decomposition of *tert*-butyl hypochlorite.

Walling suggested that problems of ring substitution might be avoided by determining the relative rates of hydrogen abstraction from 9,10-dimethylanthracene.[30] Unfortunately, this compound reacted quickly at room temperature in the absence of an initiator to form chloromethyl derivatives. Although the correct products were obtained, the rapid, spontaneous reaction of 9,10-dimethylanthracene at room temperatures precluded its kinetic study under the conditions and method of analysis used for the rest of the studies.

Unfortunately, the problems encountered with the methylanthracenes and 1-methylpyrene eliminate from the study those compounds which are potentially the most reactive. As a result, the kinetic results have only a spread of five. Conclusions drawn from such a study must be regarded as somewhat tenuous.

Since the rate-determining hydrogen abstraction step is more exothermic than the analogous reaction with the trichloromethyl radical, the transition state should assume a more intermediate position along the reaction coordinate. The reactions might, therefore, correlate better with some ground-state property or with four-parameter equation involving both the changes in π-bonding energy and the ground-state property. Table III summarizes the results of the kinetic study. The correlation of the logs of the relative rates of hydrogen abstraction with some of the parameters previously discussed are presented in Table IV.

Table III. Relative Rates of Hydrogen Abstraction from a Series of Unsubstituted Arylmethanes by *tert*-Butoxy Radical at 70°

Arylmethane	(k_X/k_O) H abstr
2-Methyltriphenylene	0.496 ± 0.048
2-Methylnaphthalene	0.599 ± 0.016
Toluene	0.601 ± 0.005
1-Methylphenanthrene	0.887 ± 0.017
3-Methylphenanthrene	0.987 ± 0.048
1-Methylnaphthalene	(1.00)
9-Methylphenanthrene	1.13 ± 0.05
1-Methyltriphenylene	1.15 ± 0.06
6-Methylchrysene	2.47 ± 0.20

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(30) C. Walling, private communication (April 10, 1970).

Table IV. Correlations of the Relative Rates of Hydrogen Abstraction from Unsubstituted Arylmethanes by *tert*-Butoxy Radical with Various Molecular Orbital Parameters

Parameter	Correlation coefficient
ΔE_π	0.739
Free valence	0.766
Atom–atom self-polarizability	0.805
$\Sigma 1/r_{ij}$	0.599

It is readily apparent that none of these parameters gives really satisfactory correlations of data. It was felt that this uniform lack of success might indicate a transition state for the reaction whose structure is truly intermediate between the arylmethane and the arylmethyl radical. Such a system might be influenced by both ground and intermediate state factors. Relative rates could be correlated by a relationship of the type shown in eq 9. Such a relationship may, however,

$$\log (k_X/k_O) = A(-\Delta E_\pi) + B(\text{ground-state property}) + C \quad (9)$$

be spurious. Often any seeming improvement is an artifact resulting from the extra variables available.[31] Let it suffice to say that none of the possible four-parameter equations generated by the data led to a really satisfactory relationship. These essentially negative findings can be interpreted to imply that the transition state occupies a position intermediate between the reactants and products along the reaction coordinate. Owing to its intermediate nature, however, the position of the transition state will probably be greatly affected by the specific steric, electronic and solvent effects of the individual arylmethanes. Hence, while trends may be discussed, a good correlation would be fortuitous.

Experimental Section

The parent arenes, toluene, 1-methylnaphthalene, 2-methylnaphthalene, and 9-methylanthracene, were obtained by purchase. The remaining nine arylmethanes, 9,10-dimethylanthracene, and *tert*-butyl hypochlorite were synthesized using standard procedures from the literature. In all cases purity was greater than 98%. The relative rates of disappearance were obtained using the usual competitive procedures.[10,32]

The Product Study of the Reaction of 1-Methylnaphthalene and Bromotrichloromethane. A solution of 14.14 mmol of 1-methylnaphthalene, 156 mmol of bromotrichloromethane, and 3.54 mmol of benzoyl peroxide was treated at 70.0 ± 0.1° in a sealed ampoule under a reduced pressure of nitrogen for 16 hr. The reaction mixture was then hydrolyzed by stirring and refluxing with 1 *N* sodium hydroxide After an insoluble yellow solid, weighing 0.169 g, was removed by filtration, the organic and basic layers were separated. After drying, the residue from the organic layer weighed 1.659 g. Glc showed that this material consisted of 55.9% 1-methylnaphthalene, 4.7% 1-naphthaldehyde, and 39.4% 1-naphthylmethanol. The amounts of each were 6.22, 0.52, and 4.38 mmol, respectively. The basic layer contained 1.09 mmol of a mixture of 1-methylnaphthalenecarboxylic acids. The material balance was 87% and the amount of reaction going by way of ring substitution was 8%.

1-Naphthaldehyde was identified by its nmr spectrum and its DNPH derivative which melted at 256–257° (lit.[33] mp 254°). The nmr spectrum of 1-naphthylmethanol in deuteriochloroform consisted of a complex aromatic absorption centered at δ 7.2, a methylene singlet at 4.8, and a singlet at 3.5 for the hydroxyl proton. It melted at 63–64° (lit.[34] mp 64°). The acids were converted to their methyl esters. The nmr spectrum of this mixture in deuteriochloroform consisted of a complex aromatic absorption centered at 7.6, a singlet at 5.6 for the methoxy protons, and a singlet at 2.6 for the methyl protons.[35] The insoluble yellow solid probably arose from attack on the substrate from phenyl radical generated in the decomposition of the initiator.[36]

The Reaction of 1-Methylpyrene with *tert*-Butyl Hypochlorite. Upon addition of *tert*-butyl hypochlorite to benzene solutions of 1-methylpyrenc and trichloroethylene at room temperature, an insoluble precipitate began to form. Precipitation was complete after about 3 min and virtually all of the 1-methylpyrene had been consumed. The products were not identified, but were assumed to be ring-substituted chlorides analogous to products formed by *tert*-butyl hypochlorite with the methylanthracenes.

Product Study of the Reaction of 9-Methylanthracene and *tert*-Butyl Hypochlorite. Benzoyl Peroxide Initiation. A solution of 8.24 mmol of 9-methylanthracene, 3.49 mmol of trichloroethylene, 10 mmol of *tert*-butyl hypochlorite, 0.209 mmol of benzoyl peroxide, and 109 mmol of benzene was treated at 70.0 ± 0.1° in a sealed ampoule under a reduced pressure of nitrogen for 160 min. After completion of the reaction, the solvent and residual *tert*-butyl hypochlorite were removed, the residue was redissolved in ether, and the mixture hydrolyzed by stirring and refluxing with 0.2 *N* sodium hydroxide. The product consisted of 75% 10-chloro-9-methylanthracene and 25% 9-anthrylmethanol. 10-Chloro-9-methylanthracene was identified by its melting point, 172–176° (lit.[37] mp 179–180°), and its nmr spectrum. The spectrum consisted of a multiplet centered at δ 8.2 for the α-aromatic protons, a multiplet centered at 7.3 for the β-aromatic protons, and a singlet at 2.9 for the methyl protons. The 9-anthrylmethanol was determined by the retention time of an authentic sample made by lithium aluminum hydride reduction of 9-anthraldehyde. The nmr spectrum of 9-anthrylmethanol also helped in its identification. It consisted of a complex aromatic region centered at 7.6, a singlet at 5.5 for the methylene protons, and a singlet at 3.6 for the hydroxyl proton. Further studies showed that the relative amounts of the desired product, 9-chloromethylanthracene, and the ring-substituted product were variable and often the reaction went entirely by ring substitution. 10-Chloro-9-methylanthracene would often precipitate shortly after addition of *tert*-butyl hypochlorite, even before the ampoules were degassed and sealed.

Product Study of the Reaction of 1-Methylnaphthalene and *tert*-Butyl Hypochlorite. Benzoyl Peroxide Initiation. A solution of 8.44 mmol of 1-methylnaphthalene, 10 mmol of *tert*-butyl hypochlorite, 0.208 mmol of benzoyl peroxide, and 109 mmol of benzene was treated at 70.0 ± 0.1° in a sealed ampoule under a reduced pressure of nitrogen for 370 min After the reaction was completed, the solvent and residual *tert*-butyl hypochlorite were removed. The residue weighed 1.3315 g. Glc showed that the reaction mixture consisted of 46.5% 1-methylnaphthalene, 50.1% 1-chloromethylnaphthalene, and 3.4% of an unidentified compound which was assumed to be 1-dichloromethylnaphthalene. By determining the number of mmoles of each present, material balance was found to be 97%. 1-Chloromethylnaphthalene was identified by the retention time of an authentic sample, made by converting 1-naphthylmethanol to 1-chloromethylnaphthalene with thionyl chloride, and by its nmr spectrum. The spectrum consisted of a complex aromatic region centered at 7.6 and a methylene singlet at 4.9.

Product Study of the Reaction of 6-Methylchrysene and *tert*-Butyl Hypochlorite. Benzoyl Peroxide Initiation. A solution of 0.523 mmol of 6-methylchrysene, 0.348 mmol of *o*-dichlorobenzene, 0.116 mmol of trichloroethylene, 2.5 mmol of *tert*-butyl hypochlorite, 0.082 mmol of benzoyl peroxide, and 45 mmol of benzene was prepared. An initial sample was injected into the glc to

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[31] P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York, N. Y., 1967, p 7.

[32] G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).

[33] H. W. Ides and M. L. Dodds, *ibid.*, **60**, 854 (1938).

[34] H. F. Manske and A. E. Ledingham, *Can. J. Res., B*, **17**, 14 (1939).

[35] The above reaction was carried out to less than 50% completion to avoid any possible formation of 1-tribromomethylnaphthalene. The above stoichiometry can be interpreted as proceeding through hydrogen abstraction by phenyl radical generated from the initiator. It is felt, however, that this is unlikely in view of the much greater tendency for phenyl radical to attack in the rings of methylated naphthalenes.[36]

[36] J. M. Bonnier, M. Gelus, and R. Renards, *C. R. Acad. Sci., Ser. C*, **264**, 541 (1967).

[37] B. M. Mikoklov and M. Sh. Promysloo, *Zh. Obshch. Khim.*, **20**, 338 (1950); *cf. Chem. Abstr.*, **44**, 6408*e* (1950).

obtain a relative response of 6-methylchrysene to the internal standard, *o*-dichlorobenzene The solution was then treated at 70.0 ± 0.1° in a sealed ampoule under a reduced pressure of nitrogen for 106 min. The reaction mixture was then analyzed by glc. It was found that 0.4390 ± 0.002 mmol of 6-methylchrysene had reacted. The solvent and residual *tert*-butyl hypochlorite were then removed and the residue was dried in a vacuum desiccator at 0.05 mm for 24 hr. The mixture was then dissolved in benzene and stirred and refluxed with 1 *N* aqueous silver nitrate overnight. The resulting silver chloride was filtered, dried, and found to amount to 0.4731 mmol. An nmr spectrum of the resulting organic mixture was taken. Based on the integration of the aldehyde proton peak at 10.2 and the methylene peak at 5.84, it was found the product consisted of 24% 6-chrysenyl aldehyde and 76% 6-chrysenylmethanol. Therefore 0.5444 mmol of silver chloride should have been obtained. Hence 87% of the 6-methylchrysene consumed was accounted for by silver chloride formed. A product study using the above method was run on 1-methylnaphthalene to determine the accuracy of the method. Only 90% of the 1-methylnaphthalene consumed was accounted for by silver chloride formed. This probably defines the accuracy of the method.

Reaction of 9,10-Dimethylanthracene with *tert*-Butyl Hypochlorite. Addition of *tert*-butyl hypochlorite to a benzene solution of 9,10-dimethylanthracene and trichloroethylene at room temperature showed rapid reaction even without an initiator. About 60% of the dimethylanthracene was consumed within 85 min. After removal of the solvent and residual *tert*-butyl hypochlorite, the reaction mixture was treated with silver nitrate solution. Precipitation of silver chloride indicated that substitution had taken place at the methyl groups.

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Proton Transfer and Heavy-Atom Reorganization in Amide Hydrolysis. Valence-Isomeric Transition States[1,2]

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Abstract: The hydrolysis in protium and deuterium oxides of ten ring-substituted trifluoro-*N*-methylacetanilides, $XC_6H_4N(CH_3)COCF_3$, in basic solution proceeds by rate-determining breakdown of tetrahedral intermediate to products with water catalysis (k_1 process) at low base concentrations, with hydroxide catalysis (k_2 process) at intermediate base concentrations, and by rate-determining formation of the tetrahedral intermediate (k_a process) at high base concentrations. The k_a process yields a linear free-energy relation (slope 0.35 in H_2O) with pK_b of the leaving-group aniline for all substituents (X = p-OCH_3 to m-NO_2) and occurs 1.2–1.7 times faster in deuterium oxide than in protium oxide. The k_1 and k_2 processes, on the other hand, exhibit biphasic free-energy relations with pK_b of the leaving group, with very small slopes (0.02 and 0.09 in H_2O, respectively) for $pK_b < 9$ and large slopes (0.3 and 0.7 in H_2O, respectively) for $pK_b > 9$. Solvent isotope effects for both processes decrease with increasing pK_b, in the case of the k_2 process dropping abruptly from normal to inverse values at $pK_b \sim 9$. Breakdown of the tetrahedral intermediate proceeds along two parallel pathways with valence-isomeric transition states, one involving mainly proton transfer from catalyst to nitrogen with generation of an ammonium intermediate and the other involving mainly C–N bond cleavage to give a hydrogen-bonded anilide ion intermediate. The former is favored by "poor" leaving groups (electron donors, $pK_b < 9$) and the latter by "good" leaving groups (electron acceptors, $pK_b > 9$).

When more than one chemical bond is made or broken in the course of a molecular transformation, the individual bonding changes may be either microscopically simultaneous (*concerted* or sequential in time (*stepwise*, a *step* being passage through a single activated complex). A *concerted reaction* in solution is one for which the reaction path consists of (a) an assembly of reactants into a common region ("diffusion together") which may or may not be a "solvent cage," within which the reactants may or may not be separated by or linked together by one or more solvent molecules; (b) passage through a single activated complex, the reaction coordinate motion transforming reactant molecules into product molecules; (c) departure of the product molecules from the common region ("diffusion apart"). A *stepwise reaction* will involve (a) diffusion together; (b) passage through a series of activated complexes, separated by stable structures (*i.e.*, collections of molecules with net restoring forces for all vibrational degrees of freedom); component molecules of these intermediate structures will diffuse apart and rediffuse together before the next step in the sequence if the rate of diffusion apart exceeds the rate of the next step—otherwise, the next step will occur without diffusion apart; the last step in the sequence will produce the product molecules; (c) diffusion apart of product molecules.

The class of reactions in which proton transfer is combined in the overall transformation with the reor-

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(2) Amide Hydrolysis. IV. For part III, see R. L. Schowen, H. Jayaraman, L. Kershner, and G. W. Zuorick, *J. Amer. Chem. Soc.*, **88**, 4008 (1966).

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