a free radical chain reaction, analogous to the free radical addition of sulfonyl halides,[2] and involves alkoxysulfonyl radicals as the reactive intermediates.

Experimental Section

Materials. Methyl, methyl-d_3, ethyl, and butyl chlorosulfates were prepared by the reaction of corresponding alcohols with sulfuryl chloride.[31] 2,2,2-Trifluoroethyl chlorosulfate was prepared by the same route,[32] while trimethylsilyl chlorosulfate was obtained by the action of chlorosulfuric acid on trimethylchlorosilane.[33] The other materials used in this work were commercially available. All compounds used were carefully purified by standard procedures before use.

Techniques. The laser flash photolysis equipment[34] and modulation spectrometer[16] apparatus have been described in detail elsewhere. EPR spectra were reported on a Bruker ER 200 spectrometer equipped with an NMR gaussmeter, a frequency counter, and a standard variable-temperature device. A 1-kW high-pressure mercury lamp was used as the UV light source.

Acknowledgment. We thank Dr. A. Alberti for his advice and assistance with some of these experiments. We also thank NATO for the collaborative research grant No. 86/678.

Registry No. $HOSO_2^{\bullet}$, 32750-86-0; $CH_3OSO_2^{\bullet}$, 108472-92-0; $CD_3OSO_2^{\bullet}$, 119820-12-1; $CH_3CH_2OSO_2^{\bullet}$, 40355-87-1; $CH_3(CH_2)_3OSO_2^{\bullet}$, 119820-13-2; $CF_3CH_2OSO_2^{\bullet}$, 119820-14-3; $(CH_3)_3COSO_2^{\bullet}$, 40355-86-0; $CF_3OSO_2^{\bullet}$, 119820-15-4; $(CH_3)_3SiOSO_2^{\bullet}$, 119820-16-5; $FSO_2OSO_2^{\bullet}$, 119820-17-6; $(CH_3)_2NSO_2Cl$, 13360-57-1; CH_3OSO_2Cl, 812-01-1; $CH_3CH_2OSO_2Cl$, 625-01-4; $Et_3Si^{\bullet}$, 24669-77-0.

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Reaction of Arylmethanes and Heteroarylmethanes with the Nucleophilic Undecyl Radical[1]

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Received November 7, 1988

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 transition state. Much poorer correlations were obtained when either a carbocation or a 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. These results are suggestive of substantial negative charge development in the transition state.

Atom abstraction is one of the most common of free-radical reactions, with hydrogen being the most frequently encountered transferred species.[2] For this reason, a tremendous effort has been directed toward obtaining mechanistic insights into the factors influencing this process. The rates of radical reactions have long been known to be sensitive to the presence of polar substituents in the substrate.[3-5] This observation has been supported by recent findings.[6]

The most fruitful method for investigating the importance of polar effects in free-radical reactions has been the application of the Hammett σ–ρ equation.[7-10] Several investigations of hydrogen atom abstraction from substituted toluenes showed that electron-donating substituents enhanced the reactivity toward electrophilic abstracting agents such as halogen atoms,[10b,11,13] a variety of oxygen radicals,[12,13] and certain carbon radicals.[14-16] Analyses of kinetic results frequently show optimum correlation with σ^+ parameters. The usual explanation of this result is that the transition state of free-radical reactions include dipolar resonance structures.[7-10,17-20] In the specific case of hy-

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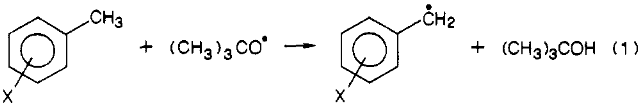
drogen atom abstraction from hydrocarbons by electrophilic radicals, the results of Hammett correlations have traditionally been regarded as being due to a contribution of the charge-separated canonical form III to the hybrid description of the transition state, which is shown below.[21]

$$\underset{\text{I}}{\text{R—H}\ {}^{\bullet}\text{X}} \leftrightarrow \underset{\text{II}}{\text{R}^{\bullet}\ \text{H—X}} \leftrightarrow \underset{\text{III}}{\text{R}^{+}\ \text{H}^{\bullet}\ :\text{X}^{-}}$$

Zavitsas and Pinto in a reexamination of hydrogen atom abstraction from substituted toluenes by *tert*-butoxyl radical (eq 1) maintained, however, that the postulation of partial charge separation in the transition state is unnecessary.[22] The observed rate enhancement found for substrates containing electron-donating groups was attributed solely to the ability of these groups to weaken benzylic carbon hydrogen bonds.



Subsequent studies have not supported that view. A consequence of the Zavitsas–Pinto approach is the prediction that only negative ρ values should be observed in hydrogen atom abstraction from substituted toluenes.[22] Several later investigations have reported positive ρ values for hydrogen atom abstraction by alkyl radicals such as *tert*-butyl,[23] isopropyl,[23b] 3-heptyl,[24] and undecyl.[25] Consequently, the resonance description of the transition state is now expanded to a hybrid of the four canonical forms shown below.[23a]

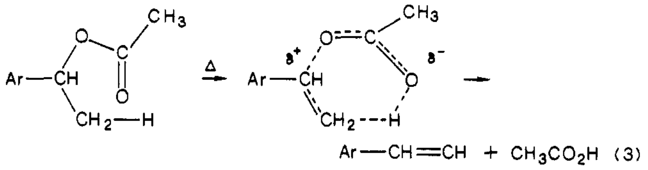
$$\underset{\text{I}}{\text{R—H}\ {}^{\bullet}\text{X}} \leftrightarrow \underset{\text{II}}{\text{R}^{\bullet}\ \text{H—X}} \leftrightarrow \underset{\text{III}}{\text{R}^{+}\ \text{H}^{\bullet}\ :\text{X}^{-}} \leftrightarrow \underset{\text{IV}}{{}^{-}\text{R}:\ \text{H}^{\bullet}\ \text{X}^{+}}$$

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.[23a]

The application of molecular orbital theory to studies involving formation and reactivity of organic free radicals has increased in the recent years.[26] It may be regarded as a complementary tool to the Hammett equation, especially in studies utilizing polycyclic substrates rather than substituted toluenes. As alternant hydrocarbon groups are inductively equivalent, this technique can allow for separation of inductive and resonance effects in free-radical reactions.[26] Examples of the above include hydrogen atom abstraction from homoarylmethanes by radicals generated from bromotrichloromethane[27] and molecular bromine,[28] addition of phenylthiyl radical to the exocyclic double bond of vinylarenes,[29] and halogen atom abstraction from halomethylarenes by triphenyltin radical.[30] It should be pointed out, however, that even though these polycyclic substrates are very amenable to simple molecular orbital correlation,[26] they do not provide any insight into the point raised by Zavitsas and Pinto.[22] Because of their alternant nature, the benzenoid systems utilized in these studies lead to parallel trends of calculated energies of the carbocation, carbanion, and radical intermediates.[31] Insight into the question of charge separation may be obtained, however, by the inclusion of heteroaromatic systems in the studies.[32,33]

In a previous paper[33] we reported our findings on the reaction of *tert*-butoxyl radical with a series of unsubstituted homoaryl- and heteroarylmethanes (eq 2). Correlation of results involved plotting the logarithms of relative rates against calculated energy differences between transition state and starting materials. Transition states were assumed to structurally resemble standard ionic or radical reaction intermediates. Calculations were carried out at the SCF-PPP level.[34] Optimum correlation ($r = 0.92$) was obtained when a carbocation transition state model was utilized. An even better correlation ($r = 0.97$) was obtained when the logarithms of the relative rates of hydrogen atom abstraction were plotted against those from the pyrolyses of the corresponding 1-homoaryl- and 1-heteroarylethyl acetates[35–37] (eq 3). This latter reaction is known to involve a transition state in which an appreciable positive charge is developed at the benzylic position. This supports the view that there is substantial positive charge development in the transition state for hydrogen atom abstraction by *tert*-butoxyl radical.

$$\text{Ar—CH}_3 + (\text{CH}_3)_3\text{C}\dot{\text{O}} \rightarrow \text{Ar—}\dot{\text{C}}\text{H}_2 + (\text{CH}_3)_3\text{COH} \qquad (2)$$



In the present paper we report the results of a study on hydrogen atom abstraction from the identical homoaryl- and heteroarylmethanes series by a nucleophilic carbon radical. The pyridine and quinoline systems utilized in this study will again provide information on the nature of charge separation possibly developed in the transition state. The abstracting species utilized is the undecyl radical. This radical is known to be nucleophilic. ρ values in the range of 0.4–0.5 have been obtained in the reaction of this species with substituted toluenes.[25] The undecyl radical (Un•) was generated by the thermolysis of lauroyl peroxide (LP) at 70 °C in an equimolar mixture of the

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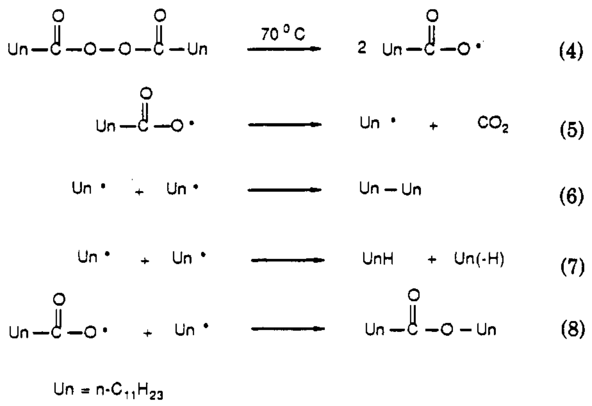
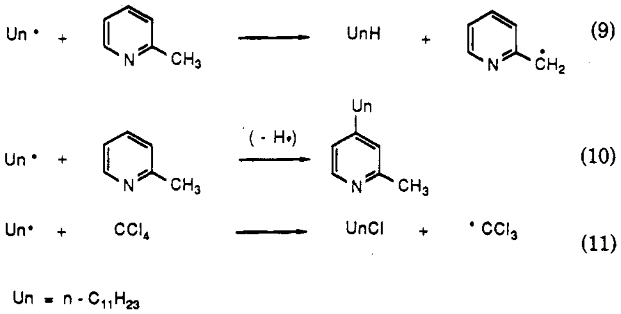
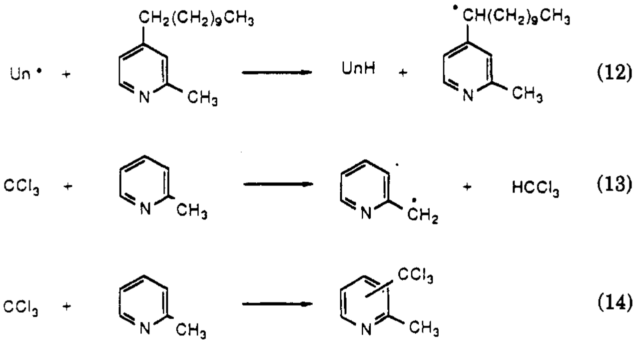
Scheme I. Initiation and Cage Reaction



Scheme II. Primary (Noncage) Product Forming Reactions (2-Methylpyridine is used as an example)



Scheme III. Secondary (Noncage) Product Forming Reactions (2-Methylpyridine is used as an example)

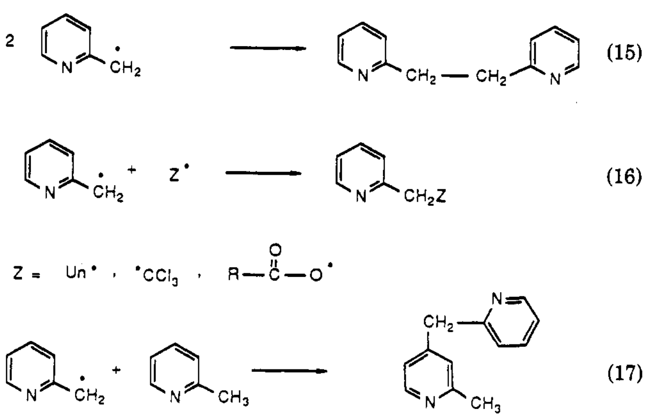


hydrogen atom donor (QH) and carbon tetrachloride. Carbon tetrachloride has been widely used as a reference in determining the relative reactivities of systems toward a variety of radicals.[15,36] Due to the complexity of the overall system, the equations for possible reaction have been divided into several schemes on the basis of their general class: Scheme I shows initiation and cage reactions, Scheme II summarizes the primary (noncage) product forming reactions, Scheme III describes the secondary (noncage) product forming reactions, and Scheme IV depicts the possible fate of the incipient benzylic radicals.

Results and Discussion

The relative reactivities of the homoaryl- and heteroarylmethanes can be determined by measuring the amounts of undecane (UnH) to 1-chloroundecane (UnCl)

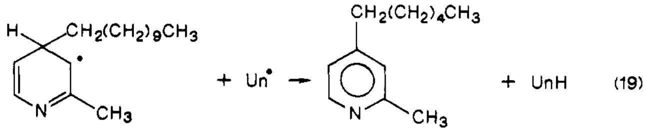
Scheme IV. Possible Fate of the Benzylic Radical (2-Methylpyridine is used as an example)



formed.[25a] The ratio of UnH to UnCl is related to k_H/k_{Cl} by eq 18. Because of possible side reactions which can

$$k_H/k_{Cl} = \frac{\text{undecane}}{\text{1-chloroundecane}} \cdot \frac{[CCl_4]}{[QH]} \qquad (18)$$

lead to the formation of undecane by hydrogen atom abstraction from secondary products, solutions of LP and donor QH in a low ratio (1:50) were utilized. Under such conditions, the possibility of induced decomposition of the starting peroxide should be minimal.[38] This would also ensure that other potential sources of abstractable hydrogen atoms, such as undecylated substrates formed via eq 12, 1,2-diarylethanes formed by the dimerization of the benzylic radical (eq 15), and diarylmethanes arising from the benzylation of substrate (eq 7) would be present in no greater abundance relative to starting substrate than 4% for the undecylated secondary products and 2% for the dimers. These secondary products would show variable benzylic hydrogen atom labilities. Diarylmethanes should be particularly prone to undergo benzylic hydrogen atom abstraction. Benzylic radicals, however, are known to undergo dimerization more readily than addition to the aromatic portion of the substrate.[39,40] Johnston and Williams[40] in the study of the reaction of *tert*-butyl peroxide with picolines and substituted toluenes have reported that the major products obtained were the coupling products with no detectable diarylmethanes being observed. Even though all these secondary benzylic systems are potential sources of undecane by hydrogen atom abstraction, the maximum concentrations mentioned above are never reached. Other products predominate even in the case of the least reactive substrate examined in this study. The presence of these secondary products should not affect the ratio of undecane to 1-chloroundecane within experimental error. While secondary products are not present in high enough concentration to appreciably affect the ratio of undecane:1-chlorodecane, hydrogen atom abstraction from the intermediate σ complexes which result in formation of undecylated substrates (eq 19) may compete with reaction under study (eq 9). Even though the



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concentration of the intermediate σ complex is never greater than that of 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 determine how this might affect the undecane:1-chloroundecane ratio, 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 utilized parent systems to undergo radical alkylation.[37] Since a mixture of reactive undecylated quinolines is being generated, the undecane:1-chloroundecane ratio must be extrapolated to zero time to obtain the inherent ability of the parent system to generate undecane. It was found that this side reaction (eq 19) can account for less than 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 uncertainty.

With regard to extraneous undecane, the most serious source is that formed in the solvent cage by the disproportionation of undecyl radicals (eq 7). The disporportionation 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. Under the reaction conditions utilized, it could be affirmed that no undecene disappeared by undergoing radical addition with the carbon tetrachloride. The product of that reaction, 1,1,1,3-tetrachorododecane was independently synthesized and shown not to be present in the reaction mixtures. The relative reactivities of the homoaryl- and heteroarylmethanes studied can now be determined by using eq 20. Undecene

$$\frac{k_H}{k_{Cl}} = \frac{(\text{undecane}) - (\text{1-undecene})}{\text{1-chloroundecane}} \cdot \frac{[CCl_4]}{[QH]} \qquad (20)$$

might also arise from a similar disproportionation between undecyl and dodecanoyloxy radical within the cage. This process, however, must be minor as dodecanoic acid was not observed among the products in nearly all of the systems studied. An exception was the 3-picoline case wherein a very small amount of this material (ca. 1% of undecane) was present.

The relative reactivities of the substrates investigated in this study are presented in Table I. All reactions 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 the hydrogen atom abstraction from the same series of compounds by *tert*-butoxyl radical.[33] Very substantial differences among positional isomers were found. In the homoarylmethane series, 1-methylnaphthalene was found to be more reactive than 2-methylnaphthalene, which was about 4 times more reactive than toluene. This reactivity order has been found for the formation of carbocation,[41] carbanion,[42] and radicals at the benzylic position.[24] With regard to the picolines, the 4-isomer was found to be more reactive than the 2-isomer, which in turn was much more reactive than the 3-isomer. This is opposite to the trend observed in the reaction of these substrates with *tert*-butoxyl radical.[33] The reactivity order obtained for the methylquinolines isomers is as follows:

$$\text{4-Q} > \text{5-Q} > \text{2-Q} > \text{7-Q} = \text{6-Q} > \text{3-Q} > \text{8-Q}$$

This is also opposite to the trend found in the reaction of these compounds with *tert*-butoxyl radical.[33] This trend suggests that partial negative charge is being developed in the transition state of hydrogen atom abstraction from homoaryl- and heteroarylmethanes by undecyl radical.

Table I. Relative Rates of Hydrogen Atom Abstraction from Homoaryl- and Heteroarylmethane by Undecyl Radical at 70 °C

system	k_H/k_{Cl}[b]	relative rates
toluene	0.031 ± 0.002[c]	1.00
3-methylpyridine	0.033 ± 0.001	1.07 ± 0.03
8-methylquinoline	0.035 ± 0.002	1.13 ± 0.07
3-methylquinoline	0.082 ± 0.001	2.65 ± 0.03
6-methylquinoline	0.096 ± 0.004	3.10 ± 0.13
7-methylquinoline	0.096 ± 0.002	3.10 ± 0.07
2-methylnaphthalene	0.135 ± 0.003	4.36 ± 0.10
2-methylquinoline	0.184 ± 0.001	5.93 ± 0.03
5-methylquinoline	0.193 ± 0.004	6.23 ± 0.13
1-methylnaphthalene	0.228 ± 0.010	7.36 ± 0.32
2-methylpyridine	0.232 ± 0.020	7.48 ± 0.65
4-methylpyridine	0.347 ± 0.005	11.2 ± 0.16
4-methylquinoline	0.463 ± 0.018	14.9 ± 0.12

[a] Number of replicate runs = 5, except for 5-methylquinoline number of runs = 3. [b] Determined by using eq 20. [c] Standard deviations.

SCF-PPP[34] calculated total energy[34,43] differences between arylmethyl intermediates and starting materials, which were considered as being equivalent to the parent unsubstituted systems, were again used to evaluate the nature of any charge being developed in the transition state. Correlations based on carbocation and radical intermediates were virtually nonexistent. The respective correlation coefficients are 0.51 and 0.10. A more reasonable correlation was obtained when arylmethyl carbanions were utilized to model the transition state. The correlation coefficient was 0.87. The modest nature of this correlation cannot be solely attributed to experimental errors. It is also possible that the calculation techniques employed do not take in account certain factors such as peri or through space interactions.[33] However, the correlation tends to support the formalism of partial negative charge development at the reactive carbon in the transition state of hydrogen atom abstraction from homoaryl- and heteroarylmethanes by the nucleophilic undecyl radical.

Due to the modest nature of the correlations discussed above, an attempt was made to correlate the rate data determined in this study with some comparable experimental results. Unfortunately, the amount of data in the literature pertinent to the formation of heteroarylmethyl carbanions is rather limited. However, such data do exist. Shatenshtein and co-workers[44] have reported the results of the lithium isopropoxide catalyzed hydrogen–deuterium exchange of methylquinolines and methylpyridines in perdueteriodimethyl sulfoxide. The base-catalyzed hydrogen–deuterium exchange of carbon acids is well known to involve a carbanion intermediate.[45,46]

A modest correlation is obtained when the logarithms of the relative reactivities for the heteroarylmethanes ob-

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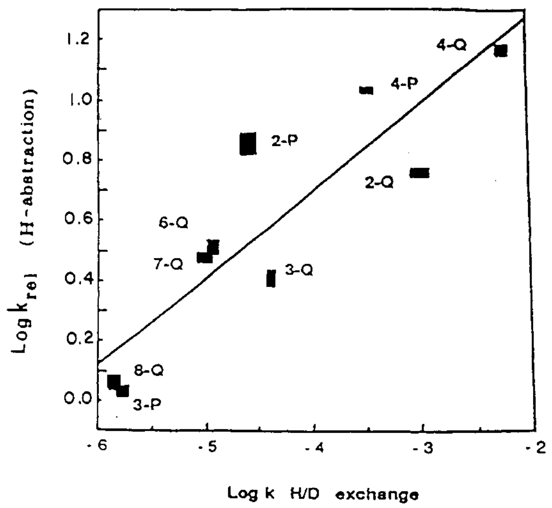

Figure 1. Logarithms of the relative rates of formation of heteroarylmethyl radical versus logarithms of the rates of base-catalyzed hydrogen–deuterium exchange of the corresponding heteroarylmethanes.

tained in the present study are plotted against the corresponding logarithms of the kinetic CH acidities reported by Shatenshtein.[44] The value of the correlation coefficient is 0.88, and the plot is shown in Figure 1. However, much better correlations are obtained when the series of heteroarylmethanes is divided into two sets: methylquinolines and methylpyridines. The correlation coefficients now obtained are 0.95 and 0.97, respectively. A justification for this is possible. Shatenshtein and co-workers have suggested that there are pronounced differences in the solvation of the carbanion intermediates generated from methylquinolines and methylpyridines.

The homoarylmethanes studied could not be included in this correlation because their acidities were determined under very different experimental conditions with regard to solvent, temperature, and the nature of the base catalyst employed.[47]

Conclusion

Although the correlation of relative rate data for hydrogen atom abstraction by undecyl radical with calculated energy differences involving a carbanion-like transition state is less satisfactory than the results reported for the corresponding *tert*-butoxyl–carbocation system, it is felt that they are supportive of the development of appreciable negative charge in the transition state. The variation in reactivity among substrates, along with the good correlations obtained with the kinetic acidities for individual series, are indicative of partial negative charge being developed at the reactive carbon of the transition state of the reaction studied.

Experimental Section

Reagents. The compounds utilized in this study were all commercially available except 5-methylquinoline. Preparation of this compound has been discussed elsewhere.[33] The purity of all compounds was determined by gas chromatography and was better than 99% in all cases.

Procedure for the Determination of Relative Rates of Hydrogen Atom Abstraction by Undecyl Radical. 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 h in a constant-temperature oil bath maintained at 70 ± 1 °C. After completion of the reaction the ampoules were cooled and opened. Aliquots (0.5 mL) of the reaction mixture were diluted to 10 mL with a 9.52×10^{-4} M solution of 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 a Varian 3300 capillary gas chromatograph equipped with an FID detector, 30 m × 0.25 mm DB-5 capillary column, and a Varian 4290 integrator. Helium was the carrier gas.

Acknowledgment. We express our gratitude to Drs. D. Camaioni and J. Franz of Battelle Northwest who generously donated certain compounds utilized in this study and to the Oregon State Computer Center, which provided the resources to carry out the calculations. Thanks are extended to the government of Algeria for providing support to M.B. at Oregon State University.

Registry No. H_2, 1333-74-0; lauroyl peroxide, 105-74-8; undecyl radical, 55101-35-4; toluene, 108-88-3; 3-methylpyridine, 108-99-6; 8-methylquinoline, 611-32-5; 3-methylquinoline, 612-58-8; 6-methylquinoline, 91-62-3; 7-methylquinoline, 612-60-2; 2-methylnaphthalene, 91-57-6; 2-methylquinoline, 91-63-4; 5-methylquinoline, 7661-55-4; 1-methylnaphthalene, 90-12-0; 2-methylpyridine, 109-06-8; 4-methylpyridine, 108-89-4; 4-methylquinoline, 491-35-0.

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