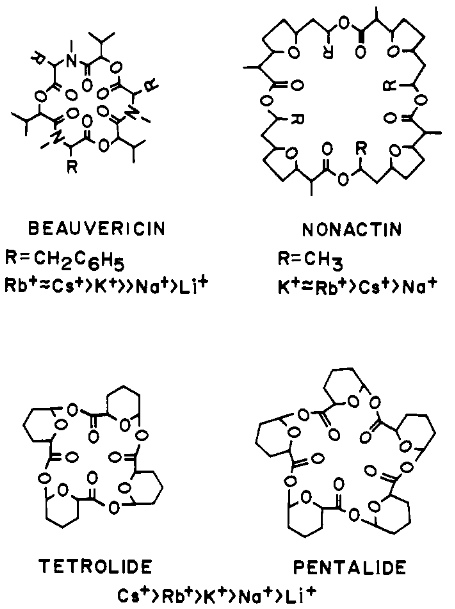

BEAUVERICIN
R=$CH_2C_6H_5$
$Rb^+ \approx Cs^+ > K^+ >> Na^+ > Li^+$

NONACTIN
R=CH_3
$K^+ \approx Rb^+ > Cs^+ > Na^+$

TETROLIDE

PENTALIDE

$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

Figure 6. Metal ion selectivity sequences of natural antibiotics (beauvericin[13] and nonactin[18]) and synthetic macrolides (**4** and **5**).

complex in which the liganding oxygens, both the heterocyclic ether oxygens and the ester carbonyl oxygens, are deployed to form the apices of a cube,[23] the complexation of beauvericin is more planar, which tends to limit its ion selectivity (K^+/Na^+ is less than 10).[13] Therefore, as described in the foregoing section, the complexation mode of **4** or **5** with a metal ion bears a striking resemblance to that of beauvericin. In addition, nonactin is a meso macrotetrolide in contrast to the synthetic macrolides **4** and **5** which are racemic compounds; in other words, the latter are chiral but not asymmetric molecules (gyrochiral molecules according to the definition by Nakazaki et al.).[24] In **4** and **5**, all the carbonyl groups are on the same side of the plane involving the macro-ring, thus making the molecule as a whole more polar than its meso counterpart having their carbonyl groups alternatingly oriented above and below the macro-ring. Therefore, these synthetic macrolides are expected to interact not only with metal cations but also with polar neutral molecules. In fact, it has recently been revealed that **4** readily forms a 1:1 molecular complex with acetonitrile, in which the acetonitrile molecule is located in the center of an approximate C_4 symmetry.[15]

In summary, the 20-membered macrotetrolide **4** and 25-membered macropentalide **5** consisting of alternating tetrahydropyran and ester moieties showed relatively low ion extraction abilities and a lyotropic sequence for alkali metal ion selectivity. They transported alkali and alkaline earth metal ions efficiently through their organic liquid membranes. In these respects, these synthetic macrolides can be regarded as model compounds for naturally occurring neutral ionophores having relatively low ion binding strength such as beauvericin. The 10-membered macrodilide **2** was totally ineffective in ion binding and ion transport.

Acknowledgment. The authors would extend their gratitude to Professor T. Ashida and his colleagues for the X-ray analysis of the cyclic oligomers. Cordial thanks are due to Dr. K. Sasaki and Dr. Y. Tarada for the calculation of conformational energy of the cyclic tetramer. Financial support from the Ministry of Education, Science and Culture, Japanese Government (Grant-in-Aid for Scientific Research No. 355392) is greatly appreciated.

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Molecular Orbital Correlations of Chlorine Atom Abstraction from Heteroarylmethyl Chlorides by Triphenyltin Radical[1]

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Abstract: A series of unsubstituted nitrogen- and oxygen-containing heteroarylmethyl chlorides was reacted with triphenyltin hydride at 70 °C in the presence of a radical initiator. The sole reaction observed was chlorine atom abstraction by the intermediate tin radical. Relative reactivity trends have been correlated with several types of self-consistent-field molecular-orbital parameters. These trends show that this reaction is not only apparently dependent upon the degree of delocalization in the intermediate heteroarylmethyl moiety, but also indicate appreciable buildup of negative charge at the exocyclic carbon atom in the transition state for chlorine abstraction.

The role played by charge-separated contributing structures to the hybrid describing the transition state for free-radical hydrogen atom abstractions has been a controversial one. Although the concept has long been accpeted, the viewpoint developed by Zavitsas and his co-workers that the negative ρ values hitherto observed in the reactions of substituted toluenes were measures solely of ground-state bond dissociation energies[2] required a reexamination of the field. The initial observation of a positive ρ value in the reaction of *tert*-butyl radical with substituted toluenes can be taken in support of charge separation.[3] Unfortunately, the view has been advanced that other (viscosity)

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(1) From the Ph.D thesis of Helene Soppe-Mbang. Initially presented at the Joint Northwest/Rocky Mountain Regional Meeting of the American Chemical Society, June 14, 1980. Reprints not available.

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factors were the cause of that positive ρ.[4] This in turn has been challenged by the original workers.[5]

In spite of the uncertainty regarding the transition state of hydrogen atom abstraction, charge separation is believed to play an important role in radical halogen atom abstractions by electropositive species. Studies utilizing trialkyl- and triaryltin radicals as abstracting agents have been particularly prominent. The view that those radical reactions could yield insight into the role played by polar effects was first put forward by Kuivila.[6] It was Grady et al., however, who carried out the initial investigation in this area by observing a positive ρ value in the reaction between substituted benzyl chlorides and the tri-*n*-butyltin radical.[7] Within the past year, this system has been reexamined and elaborated upon by Blackburn and Tanner in a major paper which extended the original work to the corresponding benzyl bromides and iodides as well.[8] Polar effects operative in the course of halogen abstraction from aryl bromides have also been recently examined by Whitesides' group and provide an important cognate study to the above by illustrating that inductive factors may act independently of delocalization.[9] Interestingly, Blackburn and Tanner reported that the reaction of benzyl iodides proceeded by a mechanism different from that of the corresponding bromides and chlorides.[8] This view has received experimental support from the results of carbon kinetic isotope effects observed by Kochi in the reaction of methyl halides with tri-*n*-butyltin radical.[10] Preliminary results on polycyclic systems in our own laboratory also tend to confirm this conclusion.[11]

The above investigations have relied upon the formalism of the Hammett equation. In so doing, a composite electronic effect including both inductive and mesomeric factors is involved. For some time we have been concerned with separating these phenomena with a particular interest of evaluating the importance of electron delocalization in radical forming processes.[12] In the past both hydrogen atom abstractions from arylmethanes[13] and addition to vinylarenes[14] had been considered. More recently a contribution has been made to the present problem under discussion in a study involving chlorine atom abstraction by triphenyltin radicals from a series of chloromethylarenes.[15]

The approach utilized in all these studies has been a straightforward one. Because alternant hydrocarbons possess uniform electron density, they may be regarded as inductively equivalent substituents which influence reactions at an adjacent exocyclic position by conjugative effects only.[16] Linear free-energy relationships between logarithms of experimental relative rate data and calculated energy differences between starting arene and transition state (usually assumed as one of the traditional intermediates) can be established. The slopes of the lines obtained in these correlations, like Hammett ρ values, are indicative of sensitivity to structural change and can provide information on probable transition-state structure. Thus, for example, the aforementioned chlorine atom abstraction yields a numerically smaller slope than the corresponding hydrogen atom abstraction when plotted against the same set of energy differences.[15] An "earlier" transition state with less radical character is presumed to be involved.

Unfortunately, the use of alternant hydrocarbon substituents is not applicable to a direct assessment of the role played by charge separation in the transition state of atom abstraction reactions. Indeed, it may be said to even obscure this role. The orbitals associated with the π electrons of alternant arenes are paired.[16] This necessitates that the corresponding arylmethyl systems show a nonbonding ortibal and that the anions, cations, and radicals derived from the same be qualitatively subjected to equivalent delocalization effects.[17] Equally reliable correlations can be obtained for both the radical and anion transition-state models. Even the results based on an implausible transition state resembling a carbonium ion is statistically equivalent. Any differences among slopes are representative of an attenuation factor reflective of varying occupancy of the nonbonded orbital and provide no basis for evaluating charge separation.

A second important point should also be made. Recent calculations from these laboratories have made use of a "total energy" approach utilizing both π energies and the σ energies of the conjugated bonds. The latter are determined as part of the interative evaluation of variable resonance integrals by means of a thermocycle.[18] In those systems, such as pyrrole, furan, and thiophene, where the partners in a bond do not make an equal contribution of π electrons, determination of the necessary terms in the thermocycle is not trivial. It can be shown, however, that results based on simple π energy calculations are quite comparable to those found from the more advanced technique for both the likely transition-state models. It is felt that the use of the former approach will introduce no major error in the correlation of data.

The use of heteroaromatic systems can provide support for the view that appreciable charge separation is involved in the transition state for chlorine atom abstraction by organotin radicals. These systems, being nonalternant, will not show the nondependence upon transition-state structure observed in the above situation. In view of this potential value, it is surprising to note that relatively few systematic investigations attempting to utilize molecular orbital formalisms to correlate the rates of formation of heteroarylmethyl intermediates exist in the literature. The most extensive study to date is that of Taylor and co-workers on the pyrolyses of 1-heteroarylethyl acetates.[19] Their original contention was that the optimum correlation of their data is achieved with a ground-state parameter (charge density) as determined by Hückel calculations.[19a,b] While this perference has been questioned,[20] the Taylor work is highly encouraging in showing the potential of MO techniques for the correlation of this type of heteroaromatic reactivity data.

Table I shows the relative rate data obtained for chlorine atom abstraction from a series of unsubstituted chloromethylheteroaromatics. Preliminary experiments showed that the disappearance of these compounds is due solely to halogen abstraction. Triphenyltin radicals have apparently no tendency to substitute into heteroaromatic rings such as pyridine and furan. In direct competition between these systems and benzyl chloride, no reaction of the former could be detected during experiments in which 95% of the latter was consumed. The product methylheteroaromatics were similarly shown to be unreactive under the conditions employed. Electron delocalization in the intermediate species appear to be very important. A comparison between 2-(chloromethyl)furan and its saturated analogue, 2-(chloromethyl)tetrahydrofuran, shows the former to be 30 times more reactive.

All measurements were run competitively in replicate at 70 °C. Reaction times varied from 1 to 4 h, which corresponds to between 15% and 80% disappearance of starting material. Reaction progress was monitored by proton NMR spectroscopy and consisted in determining the areas of benzylic protons relative to those

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Table I. Relative Rate of Chlorine Atom Abstraction from Heteroarylmethyl Chlorides by Triphenyltin Radical at 70 °C

system	no.	no. of runs	rel rates	$\Delta\Delta E_\pi$-(radical)[a]	$\Delta\Delta E_\pi$-(anion)[a]	$\Delta\Delta q$[b]
phenyl	1		1.00	0	0	0.0
2-naphthyl	2	7	1.88 ± 0.11	0.076	0.186	0.0
1-naphthyl	3	7	3.29 ± 0.48	0.175	0.571	0.0
9-phenanthryl	4	6	3.79 ± 0.24	0.178	0.605	0.0
1-anthracyl	5	6	7.95 ± 0.20	0.340	0.807	0.0
9-anthracyl	6	7	38.68 ± 2.19	0.519	1.653	0.0
2-pyridyl	7	7	1.16 ± 0.09	0.236	0.111	−0.121
3-pyridyl	8	6	1.13 ± 0.09	0.281	−0.025	0.044
4-pyridyl	9	6	2.22 ± 0.31	0.261	0.187	−0.057
2-furanyl	10	5	3.45 ± 0.45	0.525	0.050	0.057
3-furanyl	11	6	0.54 ± 0.09	0.363	−0.640	0.031
2-benzofuranyl	12	7	4.15 ± 0.06	0.565	0.480	0.039
3-benzofuranyl	13	5	1.80 ± 0.06	−0.426	−0.315	0.038
1-dibenzofuranyl	14	6	2.91 ± 0.12	0.383	0.176	0.028
2-dibenzofuranyl	15	5	3.41 ± 0.09	0.387	0.341	−0.008
3-dibenzofuranyl	16	7	2.32 ± 0.06	0.359	0.063	0.014
1-dibenzo-*p*-dioxinyl	17	6	2.09 ± 0.05	0.359	0.095	0.021
2-dibenzo-*p*-dioxinyl	18	6	2.16 ± 0.04	0.519	0.269	0.003

[a] π energies expressed relative to that of the appropriate benzene–benzyl system. [b] Relative to the charge density found at a carbon atom in any alternant hydrocarbon (1.00).

Table II. Correlation of Relative Rate Data for Chlorine Atom Abstraction from Heteroarylmethyl Chlorides, Using Molecular Orbital Parameters

system	model	slope of correlation	correl coeff[a]	SD[b] of the regression
1. heteroaromatic systems only	ΔE_π, radical TS	1.24 ± 0.62	0.532	0.148
2. heteroaromatic systems only	ΔE_π, anion TS	0.67 ± 0.16	0.803	0.115
3. heteroaromatic systems only	Δq	0.76 ± 1.55	0.153	0.176
4. all points	ΔE_π, radical TS	1.03 ± 0.57	0.411	0.244
5. all points	ΔE_π, anion TS	0.76 ± 0.05	0.929	0.115
6. all points	four-parameter ΔE_π (radical) and Δq	1.01 ± 0.53	0.426	0.370
7. all points	four-parameter ΔE_π (anion) and Δq	1.00 ± 0.08	0.951	0.126
8. all points	four-parameter ΔE_π (radical) and ΔE_π (anion)	1.00 ± 0.07	0.961	0.113

[a] Correlation coefficient. [b] Standard deviation.

of an unreactive internal standard. The formation of product methylheteroaromatics could also be observed spectroscopically. Material balance on all samples was 98.4 ± 9.5%. The compounds investigated were derivatives of pyridine, furan, benzofuran, dibenzofuran, and dibenzo-*p*-dioxin. Attempts to study (chloromethyl)quinolines and isoquinolines had to be temporarily put aside due to apparent self-reaction of these systems. For purposes of comparison, Table I also contains the previously published relative rate data for the carbocyclic systems.

The overall range of reactivities encountered for the heteroaromatic systems is somewhat smaller than that observed for the corresponding homoaromatics. Among these compounds, the most and least reactive systems differ only by a factor of 8 as compared with a factor of nearly 40 for the latter. Several of the points, namely, the derivatives of dibenzofuran and dibenzo-*p*-dioxin, are closely grouped together. All these compounds have the reaction site attached to a carbocyclic ring and, hence, quite removed from the heteroatom. The nonheterocyclic 4-phenoxybenzyl chloride system shows a relative rate of 2.32 ± 0.04, which is quite similar to the above rate.

The furan, benzofuran, and pyridine derivatives studied, on the other hand, have the reactive center directly attached to the heterocyclic ring. In the furanyl as well as the benzofuranyl derivatives, reactivity is greater for a chloromethyl group in a position α rather than β to the oxygen. This is particularly true for furan. The 2-derivative can be thought of as being more stabilized by resonance (and possible inductive) effects than the 3-derivative. The order of reactivity observed for the (chloromethyl)furans is identical with that reported by Taylor for the pyrolysis of 1-(2-furanyl and 3-furanyl)ethyl acetates.[21] The similar order of reactivity observed for the furan derivatives in both processes probably reflects the extremely important role played by delocalization in the transition states.

For the benzofuranyl compounds, the 2-chloromethyl compound, which can achieve greater stabilization by inductive and resonance effects, is again more reactive than the 3-isomer with regard to chlorine abstraction. However, the difference in reactivity between the 2- and 3-isomers here is far less than that found in furan. This is explicable in terms of the extra delocalization caused by the annellated benzene ring. Amin and Taylor have also studied the pyrolysis of 1-(2-benzofuranyl and 3-benzofuranyl)ethyl acetates.[19d] Their ratio of relative reactivity is opposite to ours (0.42 vs. 2.33). This could be explained on the rationale of opposite charge being developed in the transition state of the two processes. Such inductive effects seem to be less important than delocalization factors. Were this not so, a similar reversal of reactivity order would have also been observed for the furans. Noyce has carried out a study on the solvolysis of a series of 1-arylethyl *p*-nitrobenzoates which included 2- and 3-benzofuranyl among the aryl groups.[22] The ratio of relative reactivities for these systems is only slightly smaller than 1 (0.97). The divergence from the results of Taylor probably reflects the role played by solvation of the intermediate carbonium ions in Noyce's experiments.

The relative reactivities of the three pyridyl compounds show the order 4-pyridyl > 2-pyridyl ≥ 3-pyridyl. These results, as might be expected, are opposite to those reported by Taylor[19a] for the pyrolysis of 1-pyridylethyl acetates and those of Noyce and co-workers[23] for the solvolysis of 2-pyridyl-2-chloropropanes. These latter reactions, in which positive charges are developed in conjugation with the heteroaryl ring, show the 3-pyridyl derivative to be the most reactive isomer. As in the case of the

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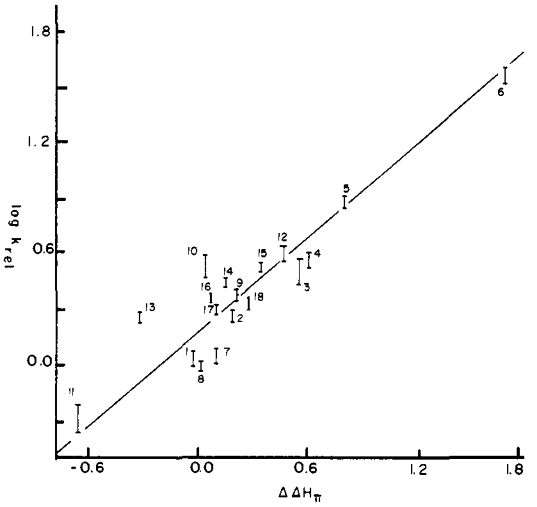

Figure 1. Logarithms of the relative rates of formation of homo- and heteroarylmethyl intermediates vs. calculated relative energy differences, using an anion transition-state model.

previously discussed benzofuran compounds, the isomeric pyridylmethyl intermediates all possess comparable degrees of resonance stabilization. The difference observed in order of reactivity between cationic and anionic like processes might again reflect the inductive nature of the heteroatom.

Table II is a compendium of the various molecular orbital correlations used to treat the present data. The appropriate values of the molecular orbital parameters are found in Table I. The first two entries reflect attempts to treat the heteroaromatic systems as a separate class of compounds by the same formalism as previously applied to the homoaromatic systems.[15] Neither correlation is particularly good. That based upon the energy differences obtained from the anion transition state, however, is appreciably better than its purely radical conterpart. The third entry represents a consideration of Taylor's approach of utilizing charge density as an appropriate ground-state parameter in treating rate data. In the present case, it yields particularly poor results.

One of the goals of the present study was to treat both homo- and heterocyclic systems in a single correlation. Entries 4 and 5 in Table II correspond to the standard energy difference approach utilizing radical and anion transition states, respectively, now applied to all systems. Again, the anion model is vastly superior. The overall correlatioin here is quite reasonable. On the other hand, the combined radical transition-state approach actually yields a poorer correlation than is found when either class of compounds is treated separately. The combined correlation using the anion transition state is illustrated in Figure 1. Because of the rather modest range of reactivities encountered for these systems, it might be legitimately argued that 9-anthracyl and 3-furanyl have an undue weight in determining the correlation. In truth, the omission of thses two points only slightly changes the value of the slope (0.76 vs. 0.67). The correlation coefficient, however, is markedly decreased in reliability (0.82).

The combined anion correlation would seem to indicate appreciable negative charge buildup in the transition state. It seems potentially productive to investigate whether other factors might play a significant role in determining the rates of the chlorine atom abstraction. Two related approaches were considered. Since the chlorine atom abstraction has been shown to have an earlier transition state than the closely related hydrogen abstraction, a correlation with a model including not only the π energy changes but also some ground-state parameters might be in order. In keeping with Taylor, we once again considered the charge density as the best ground-state parameter to use. Also, since the halogen abstraction by tin radicals has been shown to have polar character, any treatment of the transition state should thus reflect this dual radical and anionic nature. It might be instructive, therefore, to devise an equation similar to that proposed by Yukawa and Tsuno for Hammett correlation which could reflect the transition-state sensitivity to both radical and anionic factors.

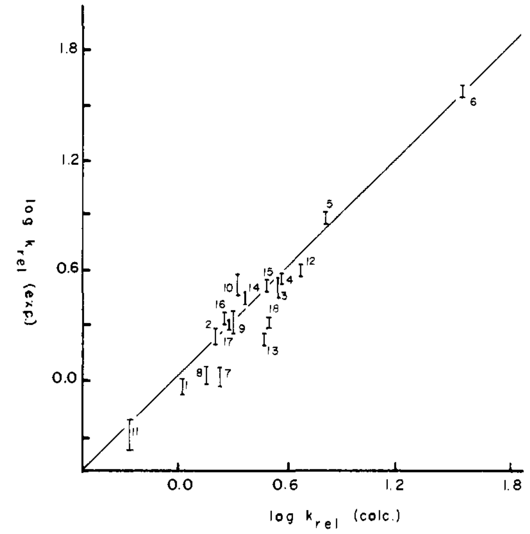

Figure 2. Logarithms of the relative rates of formation of homo- and heteroarylmethyl intermediates vs. logarithms of the calculated rates obtained from a four-parameter equation ($\Delta\Delta E_\pi$(anion) and $\Delta\Delta E_\pi$(radical)).

For testing the above approaches, four-parameter equations of the form shown in eq 1–3 were developed by curve fitting the available data.

$$\log k_{\rm rel} = 1.137\Delta\Delta E_\pi(\text{radical}) + 1.131\Delta q + 0.048 \quad (1)$$

$$\log k_{\rm rel} = 0.791\Delta\Delta E_\pi(\text{anion}) + 1.963\Delta q + 0.205 \quad (2)$$

$$\log k_{\rm rel} = 0.765\Delta\Delta E_\pi(\text{anion}) + 0.515\Delta\Delta E_\pi(\text{radical}) + 0.025 \quad (3)$$

The results of correlating these calculated rate terms against their experimental counterparts are found as entries 6–8 in Table II. As would be expected, all correlations show an approximate slope of unity. The most notable finding utilizing these equations is the extremely poor result found in the double correlation based upon raical intermediate energy differences and charge densities. It is significant that this is the only approach which completely ignores charge development in the transition state of the reaction. It might be anticipated that models employing cationic energies would be poorer still. Nearly equally good, improved correlations were found by using the other two four-parameter equations. Figure 2 shows the slightly better correlation which weas found from eq 3. This would seem to suggest a transition state which is intermediate between simple delocalized radical and anion models in its structure. The latter would also seem to be playing the larger role. The correlation resulting from the use of eq 2 must here be interpreted in slightly different terms. The use of an energy difference–charge density double correlation to treat problems in heterocyclic reactivity has already been applied to Taylor's pyrolysis results.[20] It should be most fruitful for systems having relatively early transition states. Pryor has suggested that radical processes be generally so treated by a composite model with significant ground-state contribution.[24] He cites several examples in justification. More recently, the correlation of some extremely rapid thiyl radical addition reactions have been treated by a combined transition-state–ground-state rationale.[25]

It is felt that the present findings serve two useful purposes. The data clearly support the view that the transition state for chlorine atom abstraction by tin radicals is extremely polar. The results also illustrate the utility of molecular orbital correlations as at least a cognate to more classical linear free-energy relationships.

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Table III. Syntheses of Heteroarylmethyl Chlorides

compd	method[a]	ref
7	A	
8	A	
9	A	
10	B	27, 28
11	B	27, 28
12	C	29
13	C	30
14	D	31
15	C	32
16	E	33
17	D	34
18	E	35

[a] A, chlorination of commercially available carbinol; B, because of the reported explosiveness of these compounds,[27] extremely mild chlorination conditions were employed;[28] C, from corresponding carboxylic acid; D, from hydrocarbon via lithiation and carbonation to yield acid; E, direct chloromethylation of hydrocarbon.

Experimental Section

Materials. All compounds were purified before use and exhibited physical and spectroscopic properties in agreement with literature values. GLC indicated purities in excess of 99%.

Triphenyltin hydride was prepared according to the standard method of Hoyte and Denney.[26] Because of the extreme probable lability of heteroarylmethyl chlorides, these compounds were prepared just prior to use. The general, but not exclusive, means of carrying this out was by treatment of the corresponding heteroarylcarbinol by thionyl chloride. These, in turn, were frequently obtained by lithium aluminum hydride reduction of the corresponding carboxylic acids. Table III lists the methods employed to prepare each heteroarylmethyl chloride as well as pertinent references for the syntheses of starting material.

Kinetics. Solutions of two arylmethyl chlorides, internal standard (diphenylmethane or *tert*-butylbenzene), initiator (azo*bis*(isobutyronitrile)), and benzene were prepared in approximate molar ratios of 1:1:1:0.1:100 and distributed into ampules. A small amount of the mixture was reserved for analysis of the starting material. The ampules were frozen in an acetone–dry ice slurry as soon as possible. A solution of triphenyltin hydride and benzene in the approximate molar ratio of 1:12.5 was prepared and added to the above samples. The ampules were then sealed under a reduced pressure of nitrogen and were placed in a constant temperature bath maintained at 70.0 ± 0.2 °C for times varying from 1 to 4 h. After completion of the reaction, the ampules were opened and analyzed for the disappearance of the (chloromethyl)arenes and the appearance of the arylmethanes via nuclear magnetic resonance, using the aliphatic protons of diphenylmethane or *tert*-butylbenzene as internal standards. The procedure was to have the two arylmethyl chlorides compete directly for the triphenyltin radical. Benzyl chloride was the reference compound of choice. However, when one of the arylmethyl chlorides was too reactive to compare directly with benzyl chloride, or when the benzylic protons in the two compounds overlapped, the reactivity was determined relative to some other arylmethyl chloride. The value thus obtained was converted to the desired expression by using a standard equation. Treatment of data was accomplished by utilizing standard competitive kinetic formalism.[36]

Acknowledgment. We thank Ms. Susan Randall for obtaining all NMR spectra. Appreciation is also expressed to the National Science Foundation for providing the funds for purchase of the NMR equipment and to the Computer Center of Oregon State University for providing the resources for all calculations. One of us, Helene Soppe-Mbang, also expresses her deepest gratitude to the African-American Institute for their support throughout this work.

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Flash Photolytic Triplet Sensitization and the Mechanism of Carbonylferroporphyrin Photodissociation

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Abstract: Triplet sensitization is used to examine the nature and energy of the electronic state(s) involved in photodissociation from a carbonylferroporphyrin and to study the sensitized production of the zinc porphyrin triplet state in parallel observations. Both processes are reversible over ordinary time scales, and thus we have employed a flash photolytic sensitization procedure in which the concentration of the "photoproduct" is measured in a time short compared to its lifetime, and the relative amounts generated by direct and sensitized excitation are assessed. Through the use of an appropriate suite of donors, we show that CO release occurs subsequent to triplet excitation transfer to a carbonylferroporphyrin state(s) with higher than singlet multiplicity and with energy no higher than 14 300 cm^{-1}, most probably $^3(\pi-\pi^*)$. These measurements suggest the possibility that CO photodissociation occurs via a relaxation process which proceeds through the lowest lying porphyrin $(\pi-\pi^*)$ singlet (^1Q) and triplet (^3Q) states.

Carbon monoxide photodissociation from carboxyhemoglobin has been recognized for 85 years,[1] since it was noted that exposing a mixture of oxyhemoglobin and carbon monoxyhemoglobin to solar illumination produces a marked decrease in the amount of HbCO and an increase in HbO_2.[2] Ligand photodissociation is a general property of ferrohemes and hemoproteins and has been investigated in detail, beginning with the classical series of experiments which showed that the CO heme of myoglobin photodissociates with a quantum yield of $\simeq 1$.[3] Although this

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(2) Abbreviations: HbCO and HbO_2, carboxy- and oxyhemoglobin; M(Por), metalloporphyrin; py, pyridine; TPP, tetraphenylporphyrin; DPD, deuterioporphyrin dimethyl ester.

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