(4) M. Y. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962).
(5) O. Bastiansen, F. N. Fritsh, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964).
(6) R. H. Schwendeman, G. D. Jacobs, and T. M. Krigas, *J. Chem. Phys.*, **40**, 1022 (1964).
(7) W. H. Flygare, A. Narath, and W. D. Gwinn, *J. Chem. Phys.*, **36**, 200 (1962).
(8) R. E. Long, H. Maddox, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **27**, 630 (1971).
(9) M. A. M. Meester, H. Schenk, and C. H. MacGillavry, *Acta Crystallogr., Sect. B*, **27**, 630 (1971).
(10) D. B. Chestnut and R. E. Marsh, *Acta Crystallogr.*, **11**, 413 (1958).
(11) W. Saeger and C. H. Schwalbe, *J. Org. Chem.*, **36**, 3401 (1971).
(12) J. P. Delclercq, P. Peret, and M. Van Meerssche, *Acta Crystallogr., Sect. B*, **28**, 388 (1972).
(13) C. J. Fritchie, *Acta Crystallogr.*, **20**, 27 (1966).
(14) F. R. Ahmed and E. J. Gabe, *Acta Crystallogr.*, **17**, 603 (1964).
(15) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1964).
(16) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).
(17) J. W. Lauher and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 5148 (1973).
(18) Computer programs used in this work include, in addition to local programs for the CDC 6400, local modifications of Zalkin's FORDAP Fourier summation program, the Busing-Levy ORFFE error program, Dewar's FAME program for the calculation of *E*'s, and the Main-Woolfson-Germain LSAM symbolic addition program. Our least-squares program, NUCLS, in its nongroup form, closely resembles the Busing-Levy ORFLS program. Our absorption program is AGNOST.
(19) See paragraph at end of paper regarding supplementary material.
(20) A. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).
(21) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).

Reactions of Aromatic Radical Anions. XI. Kinetic Studies of the Reaction of Sodium Naphthalene and Anthracene with *n*-Hexyl Bromide and Chloride[1]

Shelton Bank* and Donald A. Juckett

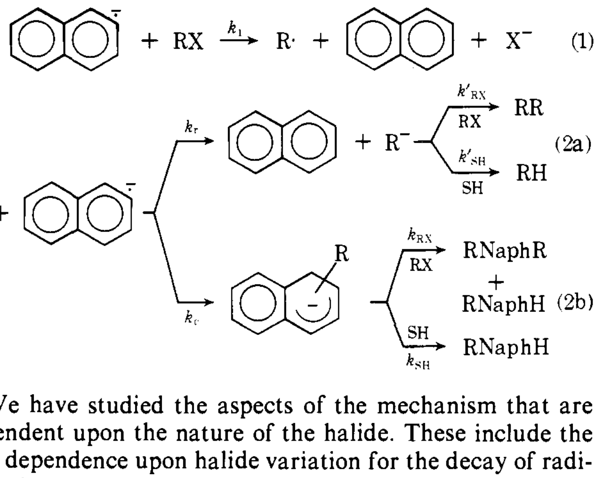
Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12222. *Received April 5, 1974*

Abstract: The kinetics were studied for the irreversible electron-transfer reaction of sodium naphthalene and anthracene with *n*-hexyl bromide and chloride. The overall second-order dependence, with first-order dependency on the aromatic anion and the halide, supports the generally accepted mechanism. The hexyldihydronaphthyl anion, however, formed from alkyl radical-radical anion coupling, is a discrete intermediate and reacts surprisingly slowly with alkyl halide. The effect of halide variation on reaction rates indicates an unusual degree of selectivity, covering a range of 11 powers of 10. The effects are similar but smaller for chromium(II) or sodium atom reduction, suggesting that the aromatic provides a special, low-energy path for electron transfer. By varying the aromatic moiety, a linear relationship was found between the half-wave potentials and the rate constants, and an extrathermodynamic relationship is considered. Ion-pairing studies reveal that the reaction is faster for loose ion pairs than for tight ion pairs. Thus although a hard localized anion is formed in the reaction, the ion-pairing effects more closely resemble those of reversible electron transfer than those of the proton-abstraction reaction. Our interpretation of the irreversible electron transfer is that it involves an early transition state with little bond breaking and charge localization on the halide.

Aromatic radical anions, although long known as reactive species, have only recently been investigated in detail. Kinetic studies of proton abstraction and reversible electron-transfer reactions have contributed to the understanding of the mechanisms and the role of solvent and counter ions in these reactions.[2-10] Of particular importance has been the elucidation of the effects of ion pairing on the kinetics of aromatic radical anion reactions.

The description of the mechanism for the irreversible electron transfer with alkyl halides has, with notable exceptions, relied primarily upon product studies.[11-15] Bockrath and Dorfman report the rates of reactions of sodium biphenyl and sodium naphthalene with alkyl iodides and bromides utilizing pulse radiolysis techniques.[16] Previously, the scope of the reactions that had been examined was confined to slow reactions utilizing conventional rate studies.[17,18]

The mechanism proposed for the reaction of sodium naphthalene with alkyl halides involves the sequence of steps 1, 2a,b. As noted previously,[11b] the important slow step involving radical anion is the initial electron transfer to the alkyl halide yielding the alkyl radical (eq 1). Since reduction (k_r) and coupling (k_c) involve the radical, for a series of halides with identical alkyl groups, the rate constants for alkyl anion and alkyl dihydronaphthyl anion formation are the same (eq 2a,b). Also the reaction of alkyl anion and alkyl dihydronaphthyl anion with solvent is independent of the halide.



We have studied the aspects of the mechanism that are dependent upon the nature of the halide. These include the rate dependence upon halide variation for the decay of radical anion and the intermediacy of the alkyl dihydronaphthyl anion. In addition the results of studies on the effect of ion pairing on reactivity and the role of various radical anions and their reactivity with alkyl halides is considered.

Results and Discussion

The Rate Law. In the mechanism outlined above, the radical anion participates in two reaction steps, the transfer of an electron to the alkyl halide and subsequent reduction of the alkyl radical and the coupling of the alkyl radical with

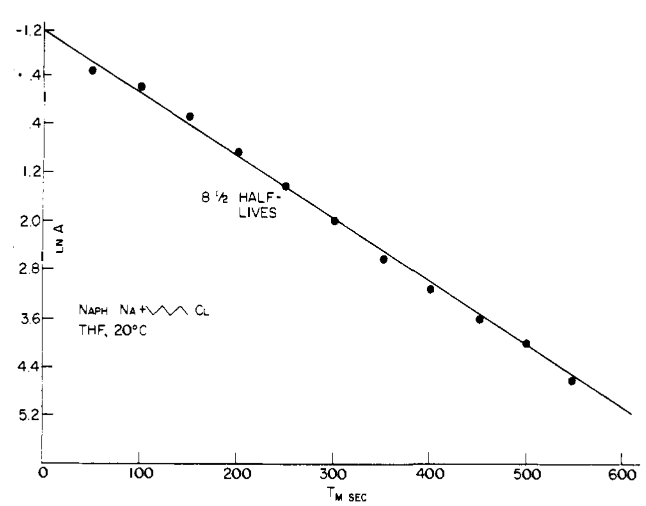


Figure 1. Pseudo-first-order plot for the disappearance of sodium naphthalene in the solution with an excess of 1-chlorohexane at 20.0°.

the radical anion resulting in the loss of radical anion. The rate expression for the change in concentration of radical anion is

$$\frac{-d[Ar\cdot^-]}{dt} = k_1[Ar\cdot^-][RX] + (k_r + k_c)[Ar\cdot^-][R\cdot] \quad (3)$$

where k_1 is the rate constant for the initial electron transfer, and k_c and k_r are respectively the rate constants for radical reduction and radical-radical anion coupling.

For the reactions of sodium naphthalene, it can be shown that the concentration of alkyl radical, [R·] in eq 3, can be treated with a steady-state approximation thereby simplifying the rate expression. The facile reduction of radicals by radical anions has been documented by several investigators.[2,3,11] For the reaction of sodium naphthalene with hexenyl halides, the rate constant for radical reaction ($k_r + k_c$) has been calculated as $\sim 2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[11,18] Since $1/(k_r + k_c)$ is shorter than reaction times, and $k_r + k_c \sim 10^9\ M^{-1}\ \text{sec}^{-1}$, the concentration of alkyl radicals generated by reaction is small and constant. These conditions are sufficient for application of the steady-state assumption to the species R·. Accordingly, the expression for the change of concentration of alkyl radicals is

$$d[R\cdot]/dt = k_1[Naph\cdot^-][RX] - (k_r + k_c)[Naph\cdot^-][R\cdot] = 0 \quad (4)$$

or

$$[R\cdot] = k_1[RX]/(k_r + k_c) \quad (5)$$

Substituting in eq 3 gives

$$-d[Naph\cdot^-]/dt = 2k_1[Naph\cdot^-][RX] \quad (6)$$

From the above expression, it can be expected that the observed kinetics will be overall second order with first-order dependence on both sodium naphthalene and alkyl halide. That the reaction is first order in radical anion can be seen from Figure 1. In an excess of alkyl halide, the reaction gives a good linear plot over 9 half-lives for the decay of sodium naphthalene. For all the kinetic runs in this work, the correlations for first-order decay of the radical anion determined by least squares are 0.98 or greater.

First-order dependence on alkyl halide was established by varying the halide concentration over an order of magnitude or more. For example, for hexyl chloride, the concentration was varied from 1×10^{-2} to 0.55 M, and multiple determinations of the pseudo-first-order rate constants were obtained at each of the six concentrations covering this range. The plot of the log of the pseudo-first-order rate constant *vs.* the log of the hexyl chloride concentration is linear with a slope of 1.06 and a correlation coefficient of 0.99 (Figure 2). Within experimental error, the slope does not vary significantly from unity, and the reaction is first order in halide. Similar data were obtained for all the halides and radical anions in this work. This first-order dependency is consistent with the first-order dependency found for alkyl fluorides in reaction with sodium naphthalene.[18]

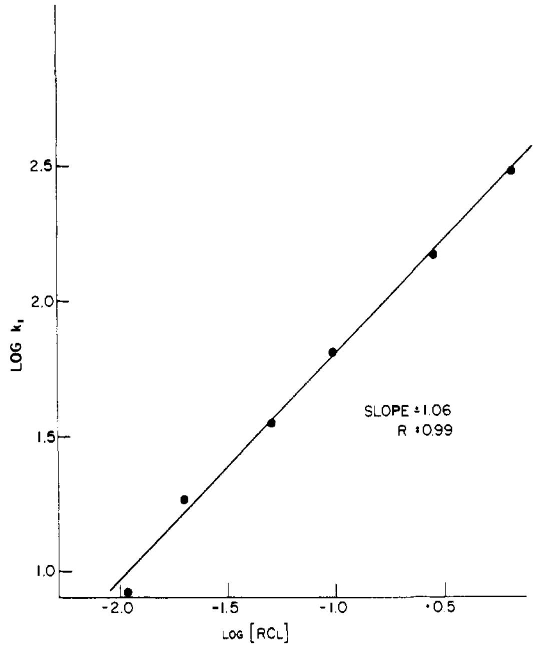


Figure 2. Plot of the log of pseudo-first-order rate constant *vs.* log of 1-chlorohexane concentration for the reaction of sodium naphthalene and 1-chlorohexane in THF at 20.0°.

Hexyldihydronaphthyl Anion (RNaph⁻). The coupling reaction of an alkyl radical with an aromatic radical anion (eq 2b) results in an alkyl dihydroaryl anion. In the reaction of sodium naphthalene with *n*-hexyl chloride, the resulting hexyldihydronaphthyl anion was examined in some detail. The rate law for the formation and decay of the hexyldihydronaphthyl anion is given as

$$d[RNaph^-]/dt = k_c[Naph\cdot^-][R\cdot] - k_{RCl}[RNaph^-][RCl] - k_{solvent}[RNaph^-][solvent] \quad (7)$$

In order to provide an accurate test for detecting the anion in the reaction, the anion was synthesized by titrating a dilute solution of sodium naphthalene in THF with *n*-hexyl chloride. The resulting red solution has a maximum at 433-435 nm and an absence of absorptions corresponding to sodium naphthalene. A minimum extinction coefficient of $1.04 \times 10^4\ M^{-1}\ \text{cm}^{-1}$ was calculated using the assumptions that $k_c/k_r = 1$, and that one quarter of the initial sodium naphthalene ends up as the hexyldihydronaphthyl anion. This value corresponds well with the extinction coefficient of $1.08 \times 10^4\ M^{-1}\ \text{cm}^{-1}$ for the dihydronaphthyl anion prepared in a similar manner.[3] The hexyldihydronaphthyl anion prepared in the above manner showed no measurable decay by reaction with solvent over a period of 140 hr, indicating that $k_{solvent}$ (eq 2b) $\ll 1 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$, and that the expression $k_{solvent}[RNaph^-][solvent]$ is very small ($\lesssim 3 \times 10^{-10}\ M^{-1}\ \text{sec}^{-1}$) at minimum concentrations of RNaph⁻ in these experiments.

The rate expression for the formation of RNaph⁻ is

$$[d[RNaph^-]/dt]_f = k_c[Naph\cdot^-][R\cdot] \quad (8)$$

where the subscript f refers to formation. Substituting the steady-state expression for [R·] yields

$$[\mathrm{d}[\mathrm{RNaph}^-]/\mathrm{d}t]_f = k_1k_c[\mathrm{Naph}\cdot^-][\mathrm{RCl}]/(k_r + k_c) \quad (9)$$

and since $k_r + k_c \sim 2k_c$, this expression reduces to

$$[\mathrm{d}[\mathrm{RNaph}^-]/\mathrm{d}t]_f \sim \frac{1}{2}k_1[\mathrm{Naph}\cdot^-][\mathrm{RCl}] \quad (10)$$

Therefore the rate of formation of the hexyldihydronaphthyl anion is proportional to the rate of decay of sodium naphthalene.

Monitoring the reaction of the hexyldihydronaphthyl anion with *n*-hexyl chloride at 435 nm yields a second-order rate constant of 4.2 M^{-1} sec^{-1} at 20°. Since the rate constants for the formation of RNaph$^-$ and the decay of Naph· are both 50 times faster than the observed rate constants, and the rate constant for the reaction of RNaph$^-$ with solvent at least 10^6 times slower than the observed rate constant, we conclude that the observed rate constant is for the reaction of the hexyldihydronaphthyl anion with *n*-hexyl chloride. Inasmuch as the reaction of sodium naphthalene with 5-hexenyl chloride yields only trace amounts of 1,5 hexadiene,[11b] we assume that the predominant reaction of the hexyldihydronaphthyl anion with *n*-hexyl chloride is a substitution reaction to yield 1,2- and 1,4-dihexyldihydronaphthalene.

The intermediacy of the hexyldihydronaphthyl anion is therefore important in the reduction of alkyl halides, and the rate at which this anion reacts with alkyl halide is surprisingly slow. In the reaction of sodium naphthalene with water, the rate of proton abstraction by the anion is much faster than by the radical anion. In contrast, in the reaction with alkyl halides, the rate of alkyl displacement is much faster by the radical anion than by the anion. Many factors can be responsible for this disparate behavior, such as steric factors. On the other hand, it is possible that the mechanism of proton abstraction by the radical anion is unique.

Reaction Rate as a Function of Alkyl Halide. The role of the halide in the reaction of sodium naphthalene with alkyl halides was investigated. With the exception of the fluorides,[18] the rates of these reactions have been too fast to measure using conventional kinetic techniques. Using pulse radiolysis techniques, Bockrath and Dorfman have measured the rate of reaction of sodium naphthalene and *n*-butyl iodide in THF solvent and have set an upper limit on the rate with *n*-butyl bromide.[16] In this study we have used rapid-mixing stopped-flow techniques to measure the rates of reaction of *n*-hexyl chloride and *n*-hexyl bromide with sodium naphthalene. Table I lists the composite rate data.

Upon examination of the rate data, it is notable that the difference in rate constants upon going from *n*-hexyl fluoride to *n*-butyl iodide is greater than 11 orders of magnitude. The agreement between the second-order rate constants for *n*-hexyl bromide utilizing stopped-flow techniques and *n*-butyl bromide using pulse radiolysis techniques allows confidence for general comparisons.

The reaction of ethylenediaminechromium(II) with alkyl halides[19] also involves alkyl radical formation in the rate-determining step with a regular progression of rate constants from chlorides to iodides. However, the relative rates are much more compressed than those for the sodium naphthalene reactions, in some cases by nearly two orders of magnitude. This could be related to the differences in the nature of the rate determining step. In the reaction of sodium naphthalene, the rate-determining step involves an electron transfer and carbon–halogen bond cleavage, while the chromium complex reactions involve halogen atom transfer to the chromium reagent.

Table I. Second-Order Rate Constants for Reaction of Sodium Naphthalene with *n*-Hexyl and *n*-Butyl Halides in THF

Alkyl halide	k_1, M^{-1} sec^{-1}	Temp, °C	Kinetic method
n-Hexyl fluoride[a]	$2.2 \pm 0.55 \times 10^{-4}$	25	Conventional
n-Hexyl chloride	$2.0 \pm 0.12 \times 10^{2}$	20	Stopped-flow
n-Hexyl bromide	$7.2 \pm 1.0 \times 10^{4}$	20	Stopped-flow
n-Butyl bromide[b,c]	$<2 \times 10^{5}$	25	Pulse
n-Butyl iodide[b,c]	$4.65 \pm 0.25 \times 10^{7}$	25	Pulse

[a] Reference 18. [b] Reference 16. [c] Dorfman and Bockrath's data corrected by dividing the published values by two to correspond with the derived rate law.

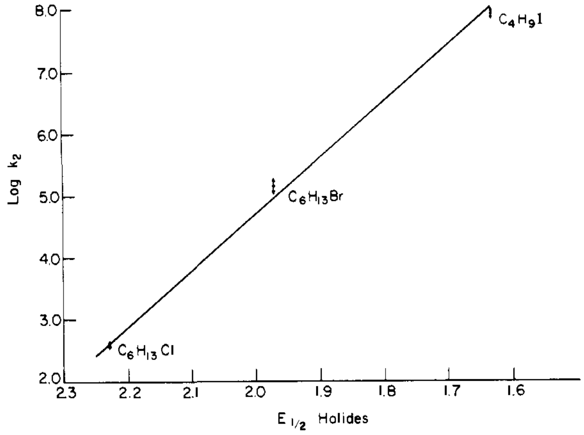


Figure 3. Second-order rate constants for the reaction of sodium naphthalene with various alkyl halides plotted against half-wave potentials for the respective methyl halides (half-wave potentials are employed to demonstrate differences in $E_{1/2}$ and are not quantitative for the alkyl halides used in these experiments).

Inasmuch as the rate-determining step for the reaction of sodium naphthalene and alkyl halides involves an irreversible electron transfer similar to the electrochemical reduction of alkyl halides, a comparison of rate constants with electrochemical half-wave potential differences of the alkyl halides was made. The plot of log k_1 as a function of the half-wave potentials (Figure 3) yields a straight line, the slope of which corresponds to a change in rate constant of 0.9 log k_1 units for each 0.1-V change in half-wave potential. The half-wave potentials of the methyl halides[20,21] were used for the rate comparisons, because it has been demonstrated that geometry as well as bond dissociation energies should be included in the expression which describes the electrode process.[21]

A comparison of the relative rate constants for the reactions of alkyl halides with sodium naphthalene and with sodium atoms[22] (Figure 4) shows good linear correlation with a slope of 1.6. The reactions are linearly related, but the slope is greater than unity indicating that the sodium naphthalene reaction is more sensitive to structural change and suggesting a later transition state with more bond breaking. This could be considered as an "intracatalytic" process where naphthalene serves as a carrier for electron transfer. An analogy would be the facilitation by naphthalene of electron transfer from an electrode surface to alkyl halides.[23]

Rate as a Function of the Aromatic Hydrocarbon. The reaction of several different aromatic radical anions with primary alkyl bromides was examined to determine the effect of the reduction potential of the aromatic upon the rate constants. A number of investigators have examined the electrochemical reductions of aromatic hydrocarbons with substantive agreement among their results.[24] Rate constants and reduction potentials for systems of interest are recorded in Table II.

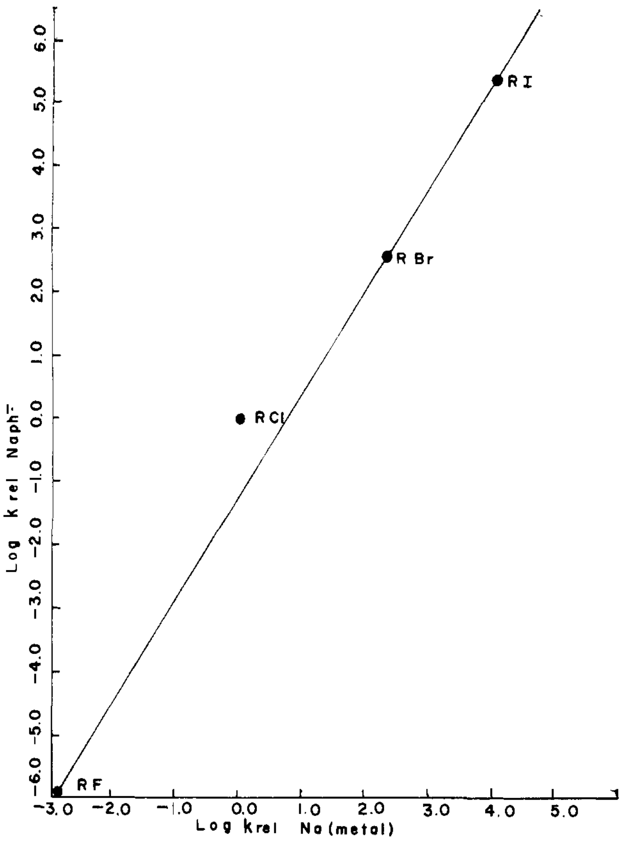


Figure 4. Log of the relative second-order rate constants of the reaction of sodium naphthalene with various alkyl halides *vs.* log of the relative second-order rate constants of sodium vapor with various alkyl halides. (The alkyl chloride for each series is arbitrarily given a K_{rel} equal to 1.)

Table II. Second-Order Rate Constants for the Reaction of Aromatic Radical Anions of Varying Reduction Potentials with *n*-Alkyl Bromides

Radical anion[a]	k_1, M^{-1} sec^{-1}	$-\epsilon_{1/2}$, V[b]
Anthracene[c]	$3.3 \pm 0.2 \times 10^2$	1.96
Naphthalene[c]	$7.2 \pm 0.1 \times 10^4$	2.50
Naphthalene[d]	$<2 \times 10^5$	2.50
Biphenyl[d]	$6.5 \pm 0.5 \times 10^5$	2.70

[a] With sodium counterion in THF. [b] *Vs.* the sce in 75% dioxane–25% water (ref 24a). [c] This work, using stopped-flow at 20° with *n*-hexyl bromide. [d] Reference 16 using pulse radiolysis at 25° with *n*-butyl bromide.

The rate range is such that a single experimental technique could not be used, and *n*-hexyl compounds were used in one study and *n*-butyl in the other. As stated earlier, the use of both techniques for the determination of similar rate constants for the reaction of alkyl bromides affords confidence in comparisons. Moreover, little differences, if any, are expected for the variation from *n*-butyl to *n*-hexyl. The second-order rate constants (Table II) increase in the order anthracene < naphthalene < biphenyl in the reaction with alkyl bromides. Comparison of these rate constants with electrochemical half-wave potentials, as in the reactions of the various alkyl halides, gives a linear correlation (Figure 5). Notably, the slope of the line corresponds to a change of 0.44 log k_1 units for a change of 0.1 V in half-wave potential. Attempts to correlate these results with the extrapolation of Warhurst's early rate data for the reaction of radical anions with alkyl halides were not successful.[27]

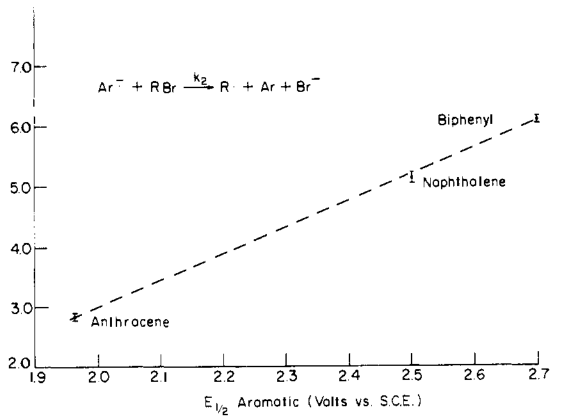


Figure 5. Second-order rate constants for the reaction of *n*-alkyl bromides with various aromatic anion radicals *vs.* half-wave potentials of the aromatics.

It has been proposed that the position of the transition state along the reaction coordinate can be estimated by an extrathermodynamic relationship between the reaction rates and the equilibrium constants.[25] In some cases, the trend between the two takes the form of an accurate linear relationship between the quantities ΔG^* and $\Delta G°$. Quantitatively, the relationship between the free energy and the activation energy is given by

$$\delta\Delta G^* = \alpha\delta\Delta G° \qquad (11)$$

A plot of ΔG^* *vs.* $\Delta G°$ will have a slope of α, where α reflects the extent to which the transition state resembles products, with a value of unity reflecting close product-like transition states and a zero value reflecting reactant-like transition states. The plot of ΔG^*, from the rate constants of the several aromatics with alkyl bromides, *vs.* $\Delta G°$, from the half-wave potentials of the aromatics, is linear with a slope of 0.22. An interpretation of these data is that for the reaction of the radical anions with alkyl bromides the transition state occurs early, and there is little bond reorganization.

A similar treatment for the half-wave potentials of the halides and the rates with sodium naphthalene gives rise to a linear plot with a slope of 0.48. This value is more complex since alkyl halides are considered to undergo reduction at an electrode surface by irreversible electron transfer concurrent with carbon–halogen bond cleavage. The reduction potentials are irreversible, and the linearity reflects a relationship between two rate phenomena. The slope considered in this way reflects a greater sensitivity to structure for the reaction at the electrode surface.

The Role of Ion Pairing. The existence of discrete ion-pairing states and the differing reactivity among these states have been examined for the reversible electron-transfer[8,26] and proton-abstraction reactions.[3] Although the effects of ion pairing in the rate-determining step are quite different for the two reactions, in both cases the effects are large. In order to ascribe significance for the study of ion pairing in this work, the irreversible electron transfer with bond cleavage, it is valuable to examine the framework for the two reactions with disparate behavior.

The existence of at least three distinct kinds of ion pairs in various ether solvents has been well documented by several investigators.[26] The equilibrium which exists in solution, represented by eq 12, is a function of solvent and temperature.

$$Na^+Naph^-_{(\text{tight})} \rightleftharpoons Na^+||Naph^-_{(\text{loose})} \rightleftharpoons Na^+ + Naph^-_{(\text{free})} \qquad (12)$$

For the proton abstraction reaction with water[3] or alcohols,[4,5] the reactivity of the tight ion pairs is greater than

Table III. Second-Order Rate Constants for the Reaction of Sodium Naphthalene and *n*-Hexyl Chloride in Various Solvents

Solvent	k_1, M^{-1} sec^{-1} $\times 10^{-2}$ [a]	Ion pairing state
THF	2.00 ± 0.12	Tight[b]
DME	10.8 ± 2.0	Loose[b]
THF-tetraglyme	12.0 ± 1.5	Glymated[b,c]

[a] At 20°. [b] References 3 and 27. [c] 50:50 by volume achieved by mixing sodium naphthalene in THF with *n*-hexyl chloride in tetraglyme.

that of the loose ion pairs. For the reversible electron transfer reaction, as for example shown in eq 13, the opposite

$$\text{Naph}\cdot^- + \text{Naph} \rightleftharpoons \text{Naph} + \text{Naph}\cdot^- \qquad (13)$$

pattern of reactivity is found, and free ions are the most reactive.[26]

A unifying concept for explaining this behavior involves the ion-pairing equilibria for the transition state complex.[27,28] To the degree that charge is dispersed in the transition state relative to the reactants, ion pairing is less important in the transition state, and the reaction is faster for the freer species. On the other hand, charge concentration in the transition state would be favored by close proximity of a counterion, and reaction is most facile for tight ion pairs. Thus the difference between the two reactions is charge dispersal between two aromatics in one case and the generation of a hard oxygen-containing anion in the other. The present system is of interest since the electron transfer involves bond cleavage and, therefore, the formation of a halide ion. The effect on ion pairing on reactivity, therefore, provides information about the degree of bond breaking and charge concentration in the transition state.

The results of solvent variation upon the second-order rate constants for reaction of sodium naphthalene with *n*-hexyl chloride, recorded in Table III, reveal an increase of nearly an order of magnitude for the glymated species relative to the tight ion pairs. This indication that the freer ion pairs are more reactive was probed more definitively by the powerful technique of temperature-dependence studies.

Sodium naphthalene in THF exists as loose ion pairs to the extent of approximately 7% at 25° and 15% at 0°.[8] Thus if the loose ion pairs are more reactive than the tight ion pairs, the effect of lowering the temperature is to increase the reaction rate. As a result, the unusual Arrhenius plot corresponds to a so-called "negative" activation energy.[26] The reversible electron-exchange reaction of sodium naphthalene and naphthalene has a "negative" activation energy,[8b,16,26] whereas reaction of sodium naphthalene with water has the usual type of Arrhenius plot.[3]

An Arrhenius plot (Figure 6) of the log of the rate constants for the reaction of *n*-hexyl chloride and sodium naphthalene over the temperature range of −16 to 50° shows the change in slope characteristic of the negative activation energy phenomenon. Clearly reaction is faster for loose ion pairs. At 10° and above, the kinetics are predominantly those of reaction of the tight ion pairs with the halide, while below −10° the kinetics of the loose ion pair predominate.

With the data in the intervening temperature region, a value for the equilibrium constant can be obtained and compared with independently obtained values. Thus at the minimum in the Arrhenius curve at 5°, we can write

$$k_{\text{tight}}[\text{Na}^+\text{Naph}\cdot^-] = k_{\text{loose}}[\text{Na}^+||\text{Naph}\cdot^-] \qquad (14)$$

and the ratio of tight to loose ion pairs is given by the ratio of the second-order rate constants. With values for these de-

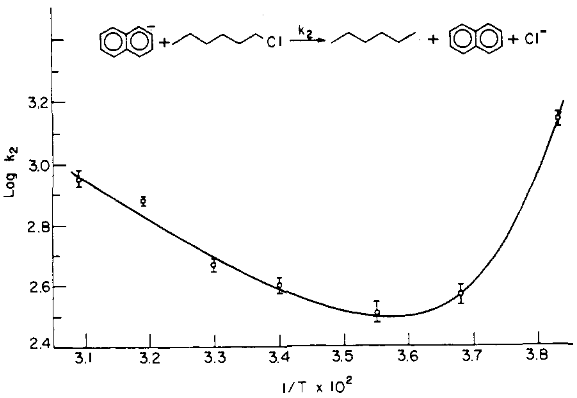


Figure 6. Arrhenius plot for the reaction of sodium naphthalene with 1-chlorohexane in THF over the temperature range −13 to 50°.

termined from the limiting portions of the curve, loose ion pairs are calculated to comprise about 15% of the mixture. This value compares favorably with the value of approximately 15% at 0° calculated from Hirota's data.[8]

The greater reactivity of the freer ion pairs has implications as to the nature of the transition state for the irreversible electron-transfer reaction. Evidently, charge is dispersed in the transition state relative to reactants, and reaction occurs with not much bond breaking and halide ion formation. In this regard, the reaction is more similar to the reversible electron exchange. Quite possibly the greater degree of bond breaking and charge development in the proton-transfer reaction is related to the fact that bond formation is required, and the transition state occurs later.

Summary and Conclusions

The kinetic order dependencies for the reaction of sodium naphthalene and anthracene with *n*-hexyl bromide and chloride support the generally accepted mechanism for the reaction of alkyl halides and aromatic radical anions. Hexyldihydronaphthyl anion is a discrete intermediate in the reaction of *n*-hexyl chloride with sodium naphthalene. This anion reacts with *n*-hexyl chloride nearly two orders of magnitude slower than does sodium naphthalene. The fact that the related dihydronaphthyl anion reacts with water at least two orders of magnitude faster than does sodium naphthalene raises questions about whether contrasting radical anion-anion reactivity patterns are related in some way or whether reactions are totally different. Delineation of this point must await further data.

The sodium naphthalene reduction of halides spans 11 powers of 10 in going from fluorides to iodides. This reduction is more sensitive to halide variation than chromium(II) or sodium atom reduction of alkyl halides. Radical anion reduction appears to be both highly reactive and highly selective. This unusual combination of reactivity phenomena may be related to an intracatalytic role for the naphthalene. Thus while the energetics of the sodium naphthalene-alkyl halide reaction are nearly as favorable as those for sodium metal and the alkyl halides, the naphthalene complex provides a low energy path for electron transfer. Related phenomena have been observed on electrode surfaces where the importance of electron transfer through the aromatic is reported.[23]

A linear relationship is observed between the half-wave potentials of the aromatics and the rate constants for reaction with *n*-alkyl bromides. In these reversible reduction potentials, an extrathermodynamic relationship is suggested with a value of α, the extent to which the transition state resembles products, equal to 0.22. This value will have to be compared with values to be determined for chlorides and io-

Table IV. Second-Order Rate Constants for Reactions of Aromatic Radical Anions and Halides

Radical anion	Solvent	Temp, °C	Halide	Concn, M	k_1, M^{-1} sec^{-1}	No. of determinations	Note[f]
Naphthalene	THF	20	n-$C_6H_{13}Cl$	1.0, 2.5, 5.2, 10.0, 25.1, and 55×10^{-2}	2.00×10^2	41	
Naphthalene	DME	20	n-$C_6H_{13}Cl$		1.08×10^3	6	
Naphthalene	THF–tetraglyme	20	n-$C_6H_{13}Cl$	2.7×10^{-2}	1.20×10^3	7	*a*
Naphthalene	THF	50	n-$C_6H_{13}Cl$	2.4×10^{-2}	4.56×10^2	7	
Naphthalene	THF	40	n-$C_6H_{13}Cl$	2.4×10^{-2}	3.84×10^2	9	
Naphthalene	THF	30	n-$C_6H_{13}Cl$	2.4×10^{-2}	2.37×10^2	7	
Naphthalene	THF	20	n-$C_6H_{13}Cl$	2.4×10^{-2}	2.00×10^2	9	
Naphthalene	THF	10	n-$C_6H_{13}Cl$	2.4×10^{-2}, 2.8×10^{-2}	1.64×10^2	9	
Naphthalene	THF	−1	n-$C_6H_{13}Cl$	2.8×10^{-2}	1.87×10^2	15	
Naphthalene	THF	−13	n-$C_6H_{13}Cl$	2.8×10^{-2}	6.98×10^2	6	
Naphthalene	THF	19	n-$C_6H_{13}Cl$	3.8×10^{-2}	2.00×10^2	7	*b*
Naphthalene	THF	19	n-$C_6H_{13}Cl$	3.8×10^{-2}	2.14×10^2	7	*c*
Naphthalene	THF	19	n-$C_6H_{13}Cl$	3.8×10^{-2}	1.91×10^2	6	*d*
Naphthalene	THF	20	n-$C_6H_{13}Br$	2.1×10^{-3}	7.2×10^4	3	
Anthracene	DME	20	n-$C_6H_{13}Cl$	2.1, 0.51	6.6×10^{-2}	19	
Anthracene	THF	20	n-$C_6H_{13}Br$	1.1×10^{-1}	3.3×10^2	10	
	DME	20	n-$C_6H_{13}Br$	2.0×10^{-1}	3.3×10^2	9	
	THF	20	n-$C_6H_{13}Br$	8.0×10^{-2}	3.1×10^2	4	*e*
	THF	20	n-$C_6H_{13}I$	1.0×10^{-2}	2.2×10^4	6	*e*

[a] THF–tetraglyme: 50:50 by volume. [b] Added Na^+ ion in the form of $NaClO_4$ to make the solution 0.025 M in added Na^+. [c] Added Na^+ ion in the form of $NaClO_4$ to make the solution 0.05 M in added Na^+. [d] Added Na^+ ion in the form of $NaClO_4$ to make the solution 0.10 M in added Na^+. [e] Sodium anthracene prepared directly from Na metal and anthracene in THF solution with an 11-fold excess of neutral anthracene. [f] Error limits for the second-order rate constants are generally ±10% or less.

dides. Application of the Hammond postulate[27] suggests a larger value for chlorides and a smaller value for iodides. The extent to which this is observed bears on the question of the amount of radical character in the several transition states.

A linear relationship is also observed between the half-wave potentials of the halides and the rates of reduction with sodium naphthalene. For these irreversible reduction potentials, such linearity relates two kinetic phenomena, namely the aromatic radical anion electron transfer and the electron transfer at the electrode surface. Reduction at the electrode surface has a greater sensitivity to halide variation.

Ion-pairing studies reveal that reaction is faster for loose ion pairs than for tight ion pairs. This is interpreted as evidence for a transition state with little bond breaking and charge localization on the halide. Tight ion pairs are expected to be favored if the hard localized anion were formed to a substantial degree in the transition state. The use of ion-pairing studies to help characterize the transition state is an interesting and important probe. Such studies may provide detailed information about the degree of charge formation in the transition state, which is not easily obtained by any other means.

Experimental Section

Materials. Naphthalene was obtained from Eastman Organic Chemicals, No. 168, or Matheson Coleman and Bell, No. NX5, and used without further purification. Alkyl halides were obtained from Eastman Organic Chemicals, purified by trap-to-trap transfer through calcium hydride, and stored cold over calcium hydride. THF, Chromoquality from Matheson Coleman and Bell, and DME, Puriss grade from Aldrich Chemical Co., were distilled from benzophenone sodium ketyl prior to use. Tetraglyme from Eastman Organic Chemicals was distilled from benzophenone sodium ketyl prior to use, bp 141° (12 mm). Purity of the alkyl halides was checked by vapor-phase chromatography. Sodium perchlorate, anhydrous from Ventron, No. 87967, was used without further purification.

Apparatus. The previously described[3] stopped-flow apparatus was used but modified by a pneumatic drive to increase reproducibility of pressure on the drive syringes. Further modifications to extend the range of observable wave lengths were accomplished by adding a photomultiplier tube with an s-1 spectral response (RCA Type 7102 photomultiplier tube). Radical anions were prepared and analyzed as previously described.[3]

Kinetic Procedures. A typical kinetic run was carried out as follows. THF (150 ml) was distilled from the sodium benzophenone ketyl under argon into the side-arm radical anion generating flask, which contained naphthalene (248 mg, 1.93 mmol), freshly cut sodium (0.5 g; 21.7 mg-atoms), and a glass-covered stirring bar. The flask was removed from the still, sealed, and allowed to stir for approximately 12 hr. The concentration was determined spectrophotometrically to be 0.0129 M from the absorbance at 365 nm.

n-Hexyl chloride (604 mg; 5.0 mmol) was carefully weighed into a small glass vial. The vial and contents were then placed in a 100-ml side-arm flask, containing a glass-covered stirring bar, which was previously flushed with argon and fitted with a septum stopper. THF (50 ml) just previously distilled from sodium benzophenone ketyl and stored under argon was introduced into the flask in a manner which excluded the entrance of air or moisture. The concentration of the n-hexyl chloride solution was calculated to be 0.10 M.

The stopped-flow apparatus, thermostated at 20°, was flushed sequentially with dry THF and then with 0.5 M sodium naphthalene until the effluent in the stop syringe retained its characteristic green color. Stock solutions of sodium naphthalene and n-hexyl chloride were transferred to the stopped-flow apparatus utilizing gas-tight syringes. After several flushes with stock solutions were made, the oscilloscope traces of six kinetic runs at 775 nm were recorded. The oscilloscope traces were photographed, and the intensities at various times were determined. The remainder of the calculations were performed by computer analysis to obtain the slope by the method of least-squares. Table IV records all the rate constants determined in this work.

Acknowledgment. We are grateful to Professor Dorfman and Dr. Bockrath for providing us with a preprint of their work. Moreover we acknowledge valuable discussions with Dr. Bockrath.

References and Notes

(1) Presented in part at the First Fall Organic Conference on Anion Activation and Catalysis, Cape Cod, Mass., Oct 1973.

(2) D. E. Paul, P. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 166

(1956).
(3) (a) S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **93**, 430 (1971); (b) *ibid.*, **94**, 6076 (1972).
(4) E. R. Minnich, L. D. Long, J. M. Ceraso, and J. L. Dye, *J. Amer. Chem. Soc.*, **95**, 1061 (1973).
(5) G. Levin, C. Sutphen, and M. Szwarc, *J. Amer. Chem. Soc.*, **94**, 2652 (1972).
(6) S. Bank and W. D. Closson, *Tetrahedron Lett.*, 1349 (1965).
(7) A. Rainis, R. Tung, and M. Szwarc, *J. Amer. Chem. Soc.*, **95**, 659 (1973), and references cited therein.
(8) (a) K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6004 (1971); (b) N. Hirota, *ibid.*, **90**, 3603 (1968); (c) A. Crowley, N. Hirota, and R. Kreilick, *J. Chem. Phys.*, **46**, 4815 (1967).
(9) R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957).
(10) R. Chang and C. S. Johnson, Jr., *J. Amer. Chem. Soc.*, **88**, 2338 (1966).
(11) (a) J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969); (b) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).
(12) (a) J. F. Garst, F. E. Barton, II, and J. I. Morris, *J. Amer. Chem. Soc.*, **93**, 4310 (1971); (b) J. F. Garst and J. T. Barbas, *Tetrahedron Lett.*, 3125 (1969); (c) *J. Amer. Chem. Soc.*, **91**, 3385 (1969); (d) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *ibid.*, **90**, 7159 (1968); (e) J. F. Garst, P. W. Ayers, and R. C. Lamb, *ibid.*, **88**, 4260 (1966).
(13) G. D. Sargent, J. N. Cron, and S. Bank, *J. Amer. Chem. Soc.*, **88**, 5363 (1966).
(14) G. D. Sargent and G. A. Lux, *J. Amer. Chem. Soc.*, **90**, 7160 (1968).
(15) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969).
(16) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, **77**, 2618 (1973).
(17) E. Warhurst and R. Whittaker, *Trans. Faraday Soc.*, **62**, 707 (1966), and previous papers in this series.
(18) J. F. Garst and F. E. Barton, II, *J. Amer. Chem. Soc.*, **96**, 523 (1974).
(19) J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970).
(20) F. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966).
(21) (a) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949); (b) M. M. Baizer, "Organic Electrochemistry," Marcel Dekker, New York, N.Y., 1973, p 282.
(22) E. Warhurst, *Quart. Rev., Chem. Soc.*, **5**, 44 (1951).
(23) A. J. Frey, "Synthetic Organic Electrochemistry," Harper & Row, New York, N.Y., 1972, p 48.
(24) (a) E. deBoer, *Advan. Organometal. Chem.*, **2**, 115 (1964), and references therein; (b) J. Jagur-Grodzinski, M. Feld, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).
(25) "When the explanation of substituent or medium effects is given in terms of similar effects in a model reaction, the quantities compared are thermodynamic, ... The simple relationships often found among such quantities are not, however, part of the formal structure of thermodynamics. Hence they are called *extrathermodynamic relationships*." This definition and an excellent discussion can be found in J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N.Y., 1963, p 128 ff.
(26) M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions," Wiley-Interscience, New York, N.Y., 1973.
(27) (a) J. G. Pacifici, J. Garst, and E. G. Janzen, *J. Amer. Chem. Soc.*, **87**, 3014 (1965); (b) J. F. Garst in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, p 570 ff.

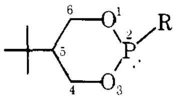
Conformations of Saturated Six-Membered Ring Phosphorus Heterocycles. III.[1] Pmr Studies of 2-Alkyl- and 2-Phenyl-5-*tert*-butyl-1,3,2-dioxaphosphorinanes

Wesley G. Bentrude,* Han-Wan Tan, and K. C. Yee

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received May 20, 1974*

Abstract: Four 2-R-5-*tert*-butyl-1,3,2-dioxaphosphorinanes were studied largely by pmr methods [R = Me (**3**), *i*-Pr (**4**), *t*-Bu (**5**), and Ph (**6**)]. Equilibration studies in solution showed that for **3**, **4**, and **6**, the cis isomer is thermodynamically more stable than the trans isomer. The ratio cis/trans *decreases* with *increasing* temperature. For **5**, the opposite is true, the trans form exceeds the cis isomer in thermodynamic stability. By far the most stable conformation for *cis*-**3**, **4**, and **6** is the chair form **9a** with 2-R axial and 5-*tert*-butyl equatorial. The axial R preference is explained in terms of optimization of vicinal interactions about the P–O bonds of the rings which are more important than repulsive 1,3-syn-axial interactions except for R = *t*-Bu (**5**). Normal steric effects are seen to be present but of secondary importance. For **5** the trans form with both ring substituents equatorial (**10a**) is the most stable. Trans-**3**, **4**, and **6** exist in chair conformers with substituents diequatorial (**10a**) but also populate conformer **10c** with substituents diaxial. These results are compared with those from earlier investigations of the corresponding 2-R-5-*tert*-butyl-1,3,2-dioxaphosphorinanes with R = Cl (**1**), MeO (**2**), Me_2N (**7**), and MeNH (**8**). Conformational free energy changes (approximate values given in text) for the conversion of R axial to R equatorial were found to be in the order CH_3O > Ph > CH_3 > *i*-Pr > MeNH > Me_2N > *t*-Bu. The first four have an axial preference. The values of J_{HP} for the equatorial 4- and 6-hydrogens of *trans*-**5** in which the phosphorus lone pair is axial show couplings to phosphorus (19.8–21.6 Hz) about twice those seen for the corresponding compounds with phosphorus lone pair equatorial. This useful configurational effect applied to *trans*-**2** rules out the population of more than 5% of form **10a** by *trans*-**2**. As much as 58% of *trans*-**2** exists in the twist conformation **10b**. Contrary to our earlier report, both cis and trans isomers of 5-*tert*-butyl-2-chloro-1,3,2-dioxaphosphorinane (**1**) are found under proper conditions of equilibration in cis/trans ratio 93/7. Findings in the 1,3,2-dioxaphosphorinanes are related to anomeric effects noted in other ring systems. Results are interpreted in terms of recent ideas concerning back bonding donations of electron lone pairs to adjacent antibonding orbitals.

That substituents CH_3O and Cl on trivalent phosphorus in 1,3,2-dioxaphosphorinanes show a preference for the axial rather than the equatorial position is well established.[2] For example, for **2** the more stable isomer is the cis chair with MeO axial and *t*-Bu equatorial, **9a**.[2a] The trans isomer exists to a large extent in a chair conformation with both substituents axial, **10c**. Phosphorochlorodite[2a] **1** also appears to be largely one isomer with *t*-Bu equatorial and Cl presumably axial, **9a**. Although such a preference is predicted by the anomeric effect[3] for electronegative substituents and noted for those substituents at the 2 position of 1,3-dioxanes,[4] the axial preference is considerably greater in the 1,3,2-dioxaphosphorinanes. For this reason, we have now studied the conformations of such rings in which phenyl and various alkyl substituents are attached to trivalent phosphorus (compounds **3–6**). These substituents are less



1, R = Cl **5**, R = *t*-Bu
2, R = OMe **6**, R = Ph
3, R = CH_3 **7**, R = Me_2N
4, R = *i*-Pr **8**, R = MeNH

Bentrude et al. / 5-tert-Butyl-1,3,2-dioxaphosphorinanes