the only isomers formed, are assigned because of the similarity of the ^{19}F chemical shifts to (*E*)-**56.**

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Nucleophilic Heteroaromatic Substitutions. XXXVIII.[1] Evidence for a Cyclic Mechanism in the Reaction of 2-Phenoxy-1,3,5-triazine with Piperidine in Isooctane

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Abstract: The kinetics of piperidino dephenoxylation of 2-phenoxy-1,3,5-triazine in isooctane have been followed spectrophotometrically. The reaction follows third-order kinetics, is not base-catalyzed, is moderately speeded up by added 2-piperidone, and proceeds by a temperature-independent rate in the range 20–70°. A sizable direct kinetic hydrogen isotope effect is observed, when piperidine-*1-d* is used, that was found to decrease as the concentration of piperidine is increased. Out of several reaction paths, the results support a cyclic mechanism involving the participation of a second molecule of piperidine acting as a bifunctional catalyst.

Much physical organic research in the field of nucleophilic substitution of nitro-activated aromatic compounds has been concerned with kinetic studies involving protic amines as nucleophiles. As reviewed recently,[2] base-catalysis studies have given valuable information about the role of tetrahedral intermediates in aromatic substitution.

In the field of aza-activated heteroaromatic substitution, extensive kinetic work has provided a quantitative evaluation of the role of the heteroatom and revealed such special-reaction features as solvent effects and acid catalysis.[3] However, little effort has been devoted to the investigation of details of the mechanism through the study of base catalysis.[4]

We now wish to report on the kinetic behavior of the reaction of 2-phenoxy-1,3,5-triazine with piperidine in isooctane (2,2,4-trimethylpentane).

A nonpolar solvent was chosen in order to minimize specific effects of the solvent upon the course of the reaction. The reaction involves the nucleophilic displacement of a fairly good leaving group from a substrate where activation is exclusively provided by the aza groups. Kinetic studies of nucleophilic substitution on monosubstituted triazine derivatives had not been reported previously; the choice of a monosubstituted triazine was intended to avoid conjugative interactions of the ring nitrogens with substituents other than the outgoing phenoxy group. We have found that, out of the reactions of several monosubstituted triazine derivatives with piperidine in a nonpolar, aprotic solvent, only that of the phenoxy derivative turned out hitherto well suited for kinetic measurements.

Experimental Section

Melting points and boiling points are uncorrected. Microanalysis was performed by "A. Bernhardt" Mikroanalytisches Laboratorium—Elbach über Engelskirchen (F.G.R.).

2-Phenoxy-1,3,5-triazine was prepared from 2,4,6-trichloro-1,3,5-triazine as described by Hirt et al.[5] and was purified by vacuum distillation and recrystallization from petroleum ether (bp

30–50°) to constant melting point [mp 59–60° (lit.[5] 59°)].

Isooctane was Merck spectroscopic grade. It was refluxed overnight upon P_4O_{10} and distilled, then stored over sodium wire.

Piperidine (Erba-RPE) for use in the kinetic measurements was purified as previously described.[1]

Piperidine-*1-d* was prepared by the method of Foster and Horman[6] and was at least 97% deuterated according to NMR analysis.

Diisopropylethylamine (Fluka) was refluxed for 2 hr over sodium and fractionated, bp 126–127° (lit.[7] 127–128°).

Quinuclidine was obtained from the corresponding hydrochloride (Aldrich) as described by Meisenheimer[8] and was purified by sublimation at 20° (2 mm), mp (sealed capillary) 158–160° (lit.[8] 158°).

Commercial (Schuchardt) **2-piperidone** (5-aminopentanoic acid lactam) was distilled before use, mp 39–40° (lit.[9] 39–40°).

2-Piperidino-1,3,5-triazine. 2-Phenoxy-1,3,5-triazine (2.00 g, 11.4 mmol) and piperidine (1.96 g, 23 mmol) were allowed to react at room temperature in benzene (6 ml), until a TLC test (Merck F_{254} silica plates, eluent: benzene–ethyl acetate 1:1) showed the complete disappearance of the starting ether (30 min). Besides phenol and piperidinotriazine, no other product was detected in the reaction mixture, either by TLC or by uv spectrophotometry. By uv spectrophotometry, no evidence was obtained for the formation of phenoxide ion in the presence of an excess of piperidine. The solvent was removed under reduced pressure at 30–35°, and the residue was taken up in chloroform. The solution was washed first with diluted sulfuric acid, then with water, and dried over Na_2SO_4. The crude product was purified by chromatography on alumina (56 g, Woelm, grade I), a mixture of petroleum ether (bp 40–70°) and benzene (9:1) being the eluent. Yield was 1.30 g (69%), mp 39–40°. Anal. Calcd for $C_8H_{12}N_4$: C, 58.51; H, 7.36. Found: C, 58.32; H, 7.28.

Kinetic Measurements. The kinetics were followed in the presence of an excess of nucleophile with respect to the substrate, by measuring the increase in absorbance at one of the absorption maxima of piperidinotriazine [λ 300 nm, ϵ_{300} (isooctane) 1.05×10^3 M^{-1} cm^{-1}]. A Perkin-Elmer Model 402 spectrophotometer equipped with a thermostated cell compartment was used. At the chosen wavelength, both the reagents and phenol do not absorb appreciably. In all cases, the absorption spectrum of the reaction mixture after several half-lives corresponded within 2% to that expected for a quantitative conversion of the reagents to the products. Reactions were started by adding 1 ml of a prethermostated stock solution of the phenoxytriazine to 2 ml of a solution either of piperidine alone or of piperidine and an added base or catalyst, contained in a 10-mm quartz cuvette which was placed in the cell compartment of the spectrophotometer. Blank experiments showed that, under the reaction conditions used in this work, neither diisopropylethylamine, quinuclidine, nor 2-piperidone reacts with the substrate nor does 2-piperidone with piperidine.

In the case of the reactions with piperidine-*1-d*, the cell compartment was flushed with a dry nitrogen stream. The concentrations of piperidine and tertiary amines were determined by acidimetry. 2-Piperidone solutions were prepared by direct weighing and diluting.

Pseudo-first-order rate coefficients were calculated as usual from plots of ln $(A_\infty - A_t)$ vs. time and converted to second-order rate coefficients, k_2, by dividing by the appropriate concentration of the nucleophile. The order of the reaction with respect to phenoxytriazine was evaluated by measuring the half-time corresponding to several initial concentrations of the substrate; the order with respect to piperidine was determined by the isolation method.[10]

Results

The reaction between 2-phenoxy-1,3,5-triazine and piperidine in isooctane yielded the expected 2-piperidino-1,3,5-triazine. No side-reaction products were detected in the reaction mixture. Among nonpolar solvents, isooctane was preferred because of its spectral transparency and sufficiently high boiling point.

The kinetics of the reaction were followed spectrophotometrically, in the presence of a varying excess of nucleophile, and gave excellent pseudo-first-order plots, without any evidence for autocatalysis phenomena. The reaction proved to be first-order in substrate. On dividing the pseudo-first-order coefficient (k_{obsd}) by the appropriate concentration of piperidine, the second-order rate coefficients (k_2) were calculated. These data are reported in Table I. The k_2 values were found to increase steadily with the piperidine concentration. Unless the piperidine concentration was higher than 0.25 M, the rate data fitted into eq 1. The slight departure from linearity at relatively high concentration of piperidine may be ascribed to a medium effect.[11] The value of the slope in expression 1 (k''') is 6×10^{-2} M^{-2} sec^{-1}, whereas the intercept of the plot (k'') falls in the proximity of the origin. Although the value of k'', as obtained by extrapolation to infinite dilution of piperidine, may be affected by serious errors, it may be estimated to be not higher than 4×10^{-4} M^{-1} sec^{-1}.

$$\text{rate}/[\text{substrate}][\text{piperidine}] = k_2 = k'' + k'''[\text{piperidine}] \quad (1)$$

Table I. Kinetic Data for the Reaction of 2-Phenoxy-1,3,5-triazine with Piperidine in Isooctane, at 41.0°[a]

[Piperidine], M	$10^5 \times k_{obsd}$,[b] sec^{-1}	$10^3 \times k_2$, M^{-1} sec^{-1}
0.0250	3.25	1.30
0.0339	5.64	1.66
0.0520	13.5	2.60
0.0660	22.7	3.44
0.0920	46.7	5.08
0.115	77.2	6.71
0.150	137	9.11
0.174	190.5	10.9$_5$
0.188	229	12.2
0.276	530	19.2
0.330	798	24.2

[a] [Substrate] = 2.90×10^{-4} M. [b] Mean values from experiments run in duplicate or triplicate.

Table II. Influence of Temperature on the Reaction of 2-Phenoxy-1,3,5-triazine with Piperidine in Isooctane[a]

Temp, °C	$10^4 \times k_{obsd}$,[b] sec^{-1}	$10^3 \times k_2$,[c] M^{-1} sec^{-1}
22.7	4.70	5.11
30.5	4.90	5.33
40.5	4.68	5.09
50.3	5.03	5.47
71.0	4.40	4.78

[a] [Substrate] = 3.11×10^{-4} M; [piperidine] = 0.092 M. [b] Mean values from duplicate runs. [c] Not corrected for solvent expansion.

At a given concentration of piperidine, increasing amounts of diisopropylethylamine or quinuclidine led to a very slight decrease in the rate of substitution (Table III).

In contrast, added 2-piperidone had a considerable rate-enhancing influence (Table IV). Accordingly, a plot of k_2 against the concentration of 2-piperidone yielded a straight line of slope 0.7 M^{-2} sec^{-1}, which is an order of magnitude greater than the slope (k''') obtained when no catalyst was added.

Kinetic hydrogen isotope effects were investigated by comparing the k_2 values for the reaction with piperidine-*1-d* with the corresponding data for the reaction with piperidine. Sizable direct isotope effects were observed (Table V).

Discussion

The kinetics of the reaction of piperidine with 2-phenoxy-1,3,5-triazine in isooctane can be represented by expression

Table III. Effect of Added Bases on the Rate of the Reaction of 2-Phenoxy-1,3,5-triazine with Piperidine in Isooctane, at 41.0°

[Diisopropylethylamine],[a] M	$10^4 \times k_{obsd}$, sec^{-1}	$10^3 \times k_2$, M^{-1} sec^{-1}
0	13.7	9.13
0.0116	13.7	9.13
0.0800	13.6	9.07
0.130	12.9	8.60
0.203	13.2	8.80
0.294	13.0	8.67
[Quinuclidine],[b] M		
0	4.88	5.30
0.0236	4.85	5.27
0.0534	4.79	5.21

[a] [Substrate] = 2.90×10^{-4} M; [piperidine] = 0.150 M. [b] [Substrate] = 3.11×10^{-4} M; [piperidine] = 0.0920 M.

Table IV. Effect of Added 2-Piperidone on the Rate of the Reaction of 2-Phenoxy-1,3,5-triazine with Piperidine in Isooctane, at 41.0°

[2-Piperidone],[a] $M \times 10^3$	$10^3 \times k_{obsd}$, sec^{-1}	$10^3 \times k_2$, M^{-1} sec^{-1}
0.92	0.741	7.10
1.6	0.844	8.09
3.5	1.001	9.59
4.2	1.048	10.05
5.3	1.445	13.85
11.1	1.52	14.57
21.8	2.065	19.80

[a] [Substrate] = 3.04×10^{-4} M; [piperidine] = 0.1043 M.

1. The second-order coefficient, k'', is at least two orders of magnitude smaller than the third-order coefficient, k'''. Therefore, according to the criterion suggested by Bunnett,[12] the reaction could be assumed to be base catalyzed. Base catalysis could be easily understood in terms of the presence of a not especially good leaving group and of the very low polarity of the solvent.

Since k'' is negligible, the reaction turns out to be third order. A similar situation was observed with nitro-activated benzenoid systems. Thus, the reaction of 2,4-dinitrophenoxybenzene with piperidine in benzene was also shown to be third order.[13]

The apparent absence of energy of activation over a wide range of temperature indicates that the reaction occurs stepwise; the rate-determining step must be preceded by at least one fast equilibrium, whereby the expected increase in rate for the slow step with increasing temperature would be compensated by a shift of the preceding equilibrium (or equilibria) toward the reagents.

According to the general mechanism of nucleophilic aromatic substitution, base catalysis occurs after the formation of a zwitterionic adduct from the substrate and one molecule of protic amine. Since rate-limiting abstraction of the acidic proton from this adduct by a base, followed by fast departure of the leaving group, must be rejected on the ground that such a process should be diffusion controlled,[14] two alternative paths have been suggested for base-catalyzed nucleophilic aromatic substitution.[2] One of them (path 1) involves a concerted abstraction of the acidic proton and departure of the leaving group (E2-like mechanism); the other (path 2) involves the rate-limiting, general-acid catalyzed decomposition of the negatively charged conjugate base of the zwitterionic adduct. In this case, the proton abstraction from the zwitterion would be a fast, specific-base catalyzed process. Path 2 may then be referred to as specific-base, general-acid (SB–GA) mechanism.

Owing to the basicity of the heterocyclic nitrogen atoms, the zwitterionic intermediate may rearrange to a neutral adduct by fast intramolecular proton transfer.[4] Phenol could then be eliminated from such an adduct (path 3).

Another possibility, which appears to be strongly supported by the present results, is as follows. The decomposition of the zwitterionic intermediate to the reaction products may be assumed to involve a transition state including two molecules of piperidine. Then, the second molecule of piperidine may act as a proton donor to the leaving group as well as a proton acceptor from the positively charged nitrogen atom of the zwitterion (path 4). A similar transition state was first proposed by Capon and Rees[15] for the substitution of 2,4-dinitrofluorobenzene by piperidine in benzene. This cyclic process is clearly related to bifunctional catalysis, as described by Bitter and Zollinger for the reaction of 2,4,6-trichloro-1,3,5-triazine with aniline in benzene.[16]

If the second molecule of piperidine were acting as a base in the rate-determining step, increasing amounts of added nonnucleophilic tertiary amines would have also brought forth an enhancement of the substitution rate. In fact, both diisopropylethylamine and quinuclidine were found to exert a weak retarding effect. We thus come to the conclusion that the reaction is not subject to general-base catalysis.[17] The origin of the retarding effect is worth a comment. It is hardly steric, because it is displayed by both bases despite their different steric requirements; instead, it is possibly related to the H-bonding interactions of the added tertiary bases with piperidine and to a resulting modification of the activity and solvating ability of the latter.

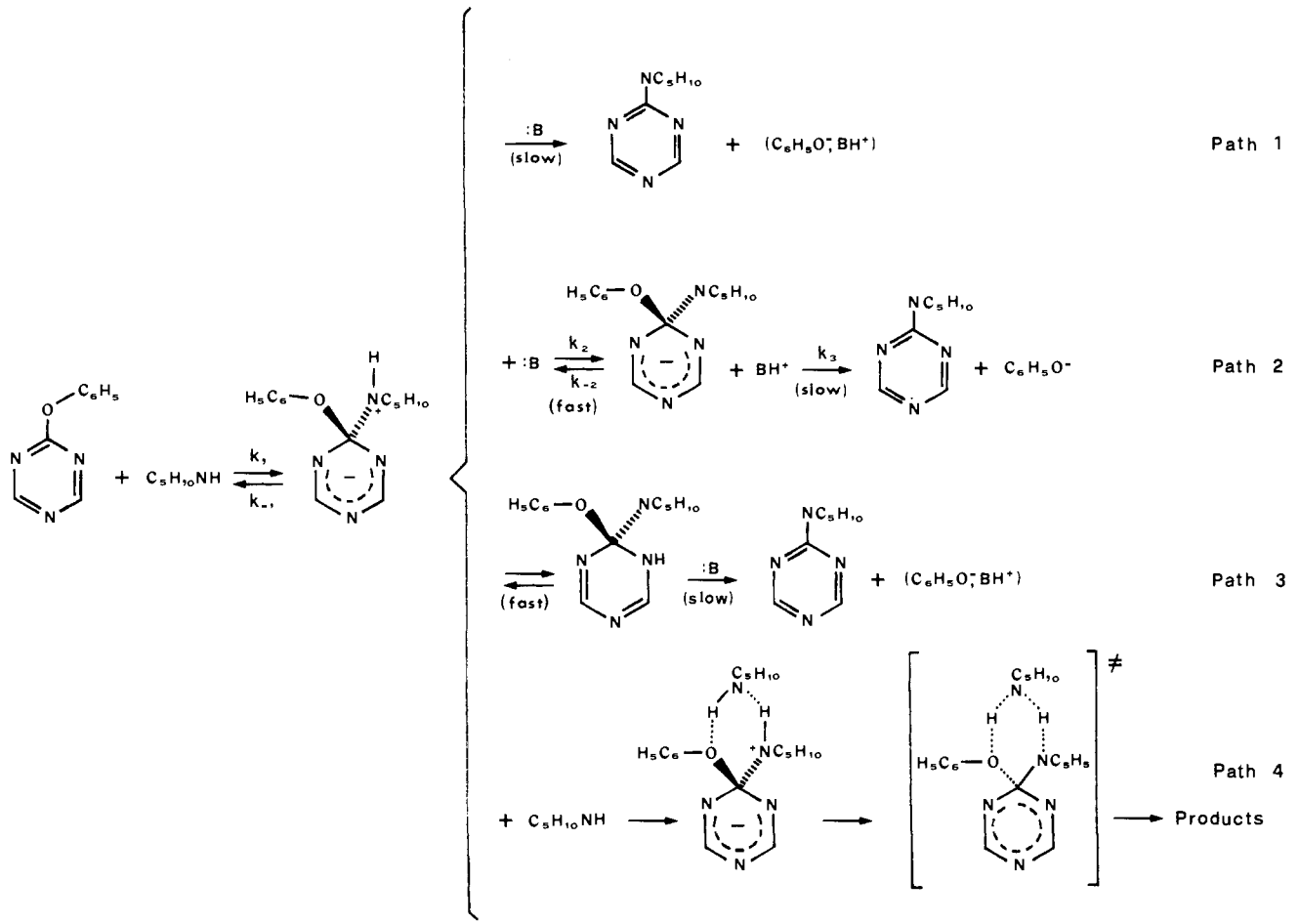
The kinetic ineffectiveness of aprotic amines seems to rule out E2-like mechanisms (paths 1 and 3), which should involve the breaking of the N–H bonds under the distinct influence of each base. Such an ineffectiveness may be still understood in the framework of a SB–GA mechanism considering that the increased efficiency of the stronger bases may be offset by the decreased catalytic effect of their conjugate acids. However, direct evidence for the SB–GA mechanism has been obtained in dimethyl sulfoxide,[18] which is a stabilizing solvent for negatively charged σ adducts.[19] The scope of the SB–GA mechanism presumably includes such hydroxylic solvents as water and methanol,[20] but quite unlikely such nonpolar, aprotic solvents as isooctane. The latter is unable to stabilize highly ionic transition states (as to path 2) and is especially suitable to promote a cyclic mechanism, which allows a nonion-generating decomposition of the zwitterionic intermediate to the products (path 4).

Another result in favor of the cyclic mechanism is the observed rate-enhancing effect of 2-piperidone, which has been found to be nearly ten times more effective than piperidine as a catalyst. Admittedly, 2-piperidone is not an ideal bifunctional catalyst, because the enolic form is less stable than the lactamic one.[21] The use of other possible bifunctional catalysts was hampered either by their reactivity or by their uv absorption, which interfered with the rate measurements. The action of 2-piperidone may be envisaged in

Table V. Kinetic Hydrogen Isotope Effect in the Reaction of 2-Phenoxy-1,3,5-triazine with Piperidine in Isooctane at 41.0°[a]

[Piperidine], M	[Piperidine-1-d], M	$10^3 \times k_2H$,[b] M^{-1} sec^{-1}	$10^3 \times k_2D$,[b] M^{-1} sec^{-1}	k_2H/k_2D
0.0826	0.0826	4.54 ± 0.1	2.24 ± 0.1	2.03 ± 0.1
0.264	0.264	18.2 ± 0.2	10.9 ± 0.2	1.67 ± 0.04

[a] [Substrate] = 3.11×10^{-4} M. [b] Mean value from duplicate runs.



the formation of an eight-membered ring in the cyclic transition state, which is expected to be more favored than a six-membered ring[22] as postulated in path 4 for the role of the second molecule of piperidine.

A comment on the acidic species present in the reaction medium is worthwhile. As the reaction progresses, phenol is expected to interact with piperidine (HNR_2) according to the following equilibria:

$$C_6H_5OH + HNR_2 \rightleftharpoons$$

$$(C_6H_5OH,\ HNR_2) \rightleftharpoons (C_6H_5O^-,\ H_2NR_2^+)$$

which seem to be markedly shifted to the left since no evidence for the formation of phenoxide ion was obtained under the conditions of the reaction (see Experimental Section). The fact that no acid autocatalysis was observed is consistent with the ring mechanism, though not unequivocally diagnostic for it.[23] However, it shows that piperidone, an acid weaker than phenol, cannot act as a merely acidic catalyst.

The kinetic hydrogen isotope effect is relatively large, as compared with those generally observed in nucleophilic aromatic and heteroaromatic substitution. This obviously means that the rate-limiting step is subsequent to the nucleophilic attack of piperidine to the substrate. Although the observed effect is not diagnostic for some of the several paths discussed above, it is of interest to note that a cyclic transition state was suggested in a preceding paper[1] also on the basis of the kinetic hydrogen isotope effects.

The kinetic isotope effect described in this paper tends to decrease as the piperidine concentration increases. For a base-catalyzed reaction, this tendency would be easily understood;[24] however, this is not the case for the reaction under examination. The observed decrease can be probably related to the different degrees of association of piperidine and piperidine-*1-d* in a nonpolar solvent, which makes the concentration of nonassociated piperidine-*1-d* lower than that of nonassociated piperidine. In fact, in nonpolar solvents, N-deuterated secondary aliphatic amines show a higher degree of association to give "dimeric," less reactive species, than the corresponding nondeuterated ones.[25]

As a final comment, we wish to point out that, in view of the dependence of the isotope effect on concentration, studies of isotope effects at different concentrations of amines, as reported in the literature, may not be strictly comparable.

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Electron-Transfer Mechanisms in Organometallic Chemistry. Alkyl Transfer from Organolead Compounds with Hexachloroiridate(IV)[1]

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Abstract: The importance of electron-transfer processes as viable routes for reactions of organometals is shown in the facile transfer of alkyl groups in the reaction between alkyllead compounds and hexachloroiridate(IV) as a model system. The rates of reaction for a series of methyl/ethyllead compounds ($Et_{4-n}PbMe_n$, $4 \geq n \geq 0$) with hexachloroiridate(IV) follow second-order kinetics. The rate constants k_2 increase progressively as methyl is replaced by ethyl groups, and a given ethyl group is cleaved more than 20 times faster than a methyl group. Both of these reactivity trends are diametrically opposed to known patterns of electrophilic cleavage. A rate-limiting step involving electron transfer from a series of organolead compounds to hexachloroiridate (i.e., log k_2) correlates with the energetics of other electron-detachment processes including: electrochemical oxidation, He I photoelectron spectroscopy, and charge-transfer bands of tetracyanoethylene complexes. Mass spectral studies indicate that selectivity in the scission of CH_3–Pb and CH_3CH_2–Pb bond arises during spontaneous fragmentation of the organolead cation radicals. Alkyl radicals are shown to be intermediates by spin trapping and the observation of the ESR spectra of nitroxide adducts. Separate experiments demonstrate that alkyl chloride arises as a product from the highly efficient scavenging of alkyl radicals by hexachloroiridate(IV). The reduced chloroiridium(III) species are partially characterized.

The formation and cleavage of carbon–metal bonds play important roles in the chemistry of organometallic intermediates involved in catalytic processes of organic as well as biochemical substrates. Transfer of alkyl groups from one metal to another can constitute the route by which alkyl groups are transported, a particularly relevant example being the cobalamin-dependent transfer of methyl groups to metals such as mercury and other heavy elements.[2]

Electrophilic processes represent by far the most common pathway by which carbon–metal bonds are cleaved, as indicated schematically in eq 1.[3] However, most organometallic

$$CH_3\text{–}M + E^+ \longrightarrow CH_3\text{–}E + M^+ \quad (1)$$

intermediates have relatively low ionization potentials, and electron-transfer processes in eq 2, as well as other efficient free-radical chain processes, are possible.

$$CH_3\text{–}M + E^+ \longrightarrow [CH_3\text{–}M\cdot{}^+E\cdot] \longrightarrow CH_3\cdot + M^+ + E\cdot, \text{etc.} \quad (2)$$

There are several reports relating to the possible importance of charge transfer in the reactions of organometallic compounds. Thus, methyl transfer in eq 3 is rapid in di-

$$CH_3\text{–}Co^{III}(acen) + Co^{II}(tfacen) \longrightarrow Co^{II}(acen) + CH_3Co^{III}(tfacen) \quad (3)$$

methyl sulfoxide and accompanied by electron transfer between cobalt(III) and cobalt(II).[4] The large number of oxidation states available to cobalt unfortunately complicates the mechanistic interpretation of alkyl transfer between those organocobalt species. Similar ambiguities are inherent in the alkyl-transfer reactions between alkylcobalt(III) and chromium(II).[5]

The oxidative cleavage of benzylbis(dimethylglyoximato)cobalt(III) by hexachloroiridate(IV) proceeds according to eq 4,[6] but it is unlikely that a benzyl radical is an in-

$$RCo^{III}(DH)_2 + 2IrCl_6^{2-} \xrightarrow[H_2O]{} Co^{III}(DH)^+ + 2IrCl_6^{3-} + ROH \quad (4)$$

termediate arising from the homolysis of the cobalt–carbon bond. For example, a related oxidative cleavage of optically active *sec*-octyl-$Co^{III}(DH)_2$ by hexachloroiridate(IV) in the presence of added bromide ion afforded *sec*-octyl bromide of inverted configuration, and nucleophilic displacement from an alkylcobalt(IV) intermediate was proposed.[7,8]

$$RCo^{III}(DH)_2 + IrCl_6^{2-} \longrightarrow RCo^{IV}(DH)_2^+ + IrCl_6^{3-} \quad (5)$$

$$RCo^{IV}(DH)_2^+ + Br^- \longrightarrow RBr + Co^{II}(DH)_2 \quad (6)$$

$$Co^{II}(DH)_2 + IrCl_6^{2-} \longrightarrow Co^{III}(DH)_2^+ + IrCl_6^{3-} \quad (7)$$

Finally, the observation of an ESR spectrum assigned to a complex between mercury and semiquinone radical was recently reported during the addition of diethylmercury to 3,5-di-*tert*-butyl-1,2-benzoquinone at 40°.[9] Homolytic cleavage of the Hg–Et bond subsequent to electron transfer was postulated, but no experimental details have appeared as yet.

We have chosen organolead compounds as models for the study of alkyl-transfer reactions, because they incorporate the best features of organometallic systems; i.e., they are reactive but sufficiently substitution stable and well behaved in solution to allow for meaningful quantitative study.[10] The intra- and intermolecular competitive cleavage of CH_3–Pb vs. CH_3CH_2–Pb bonds in a series of methyl/ethyllead compounds $(CH_3)_{4-n}Pb(CH_2CH_3)_n$ provides a useful diagnostic test for various cleavage mechanisms.[11a,b] Hexachloroiridate(IV) was chosen for its well-known properties