prepare from 2 by using tert-butyl hydroperoxide and cobalt acetate\(^{12}\) (44\%, mp 107.1–108.1 °C). With these materials in hand, it became possible to test Suttie's acylation proposal.

In these initial studies we have examined only acylations at nitrogen and oxygen. The hydroperoxide 3 undergoes an extremely smooth reaction with 1 equiv of carbonyl diimidazole (Scheme III) to form the desired quinone epoxide 7 and acetylazimidae in nearly quantitative yield. Zinc triflate is the most effective Lewis acid catalyst found to date for the formation of phenyl acetate from 3 and phenol.\(^{13}\) With other Lewis acids such as boron trifluoride, the hydroperoxide is converted to quinone epoxide 7, but no acetylation is observed. Thus, the formation of these acetylation products along with the quinone epoxide is good evidence in support of Suttie's mechanism.

It is thought that the key to success in these reactions lies in finding conditions that will restrict the availability of undesired nucleophiles which might react with the activated acetyl group. To this end we have examined conditions that might be expected to generate the desired nucleophile, alkoxy ions, simultaneously with the activated acetyl species. Desilylation of 5 with fluoride ion in the presence of benzyl bromide should lead to the peroxide 8 (Scheme III) and this species might fragment to form an alkoxy ion and active acylating agent as an ion pair 9, \(R' = C(CH_3)_3\).

The feasibility of this ion pair hypothesis is indicated by the formation of quinone epoxide 7 and benzyl acetate in nearly equivalent yields. Unfortunately, the peroxide 8 could not be detected as an intermediate. Thus, 8 would appear to be very labile in contrast to the tert-butyl peroxide 6 which is reasonably stable. The same ion pair model for acetylation succeeds with 6 when zinc triflate is used as a catalyst.\(^{13}\) In this reaction the zinc triflate might complex with the \(\alpha\)-peroxy ketone unit as shown in 10 and bias the peroxide linkage in favor of a heterolytic cleavage to form the ion pair 9, \(R' = C(CH_3)_3\).

In summary, this work has demonstrated that peroxy analogues of vitamin K are readily formed from molecular oxygen under conditions closely approximating those found in biological systems. Further, it has been shown that ionic decomposition of these peroxides does lead to active acylating species. Finally, it must be noted that phenolic esters have previously been converted to active acylating species through electrochemical\(^{15}\) and chemical\(^{16}\) means. However, this is the first demonstration of a route for coupling oxidation with molecular oxygen to acylation.

Acknowledgment. We thank Leo Geraci for assistance in the preparation of starting materials and the National Science Foundation for support of this work under Grants CHE-8004235 and CHE-8312691.

(14) The reactions described here afford simple reaction mixtures. Many other conditions examined afford complex mixtures. These intractable mixtures are possibly the result of triggering radical chain modes of peroxide decomposition.


Lithium-Metalloid Exchange Reactions. Kinetic Evidence for an Intermediate in the Lithium-Iodine Exchange\(^{1}\)

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The metal–halogen exchanges (Li/Br, Li/I)\(^{2}\) are the best known of a family of lithium–metalloid exchange reactions, of which the Li/Sn\(^{2}\) and Li/Se\(^{2}\) exchanges are also commonly used members. These reactions have achieved special importance for the preparation of functionalized and/or unstable alkyl-, vinyl-, and aryl lithium reagents.\(^{2b,2e,4}\) Kinetic studies of the Li/M exchange

(1) For a previous study of hypervalent iodine, see: Reich, H. J.; Coppe-erman, C. S. J. Am. Chem. Soc. 1973, 95, 5077.


Figure 1. Effect of iodobenzene on the rate of reaction of phenyllithium with 1-iodobutane in THF at -78 °C. The points are experimental, the line was calculated by using $k_2 = 7.0 \times 10^{-4} \text{ L mol}^{-1} \text{s}^{-1}$ (test 2) and $K = 5.9 \text{ mol L}^{-1}$ (eq 1).

![Figure 1](image1)

Table I. Results of Tests 1 and 2

<table>
<thead>
<tr>
<th>C6H5M</th>
<th>test 1 $R_1$</th>
<th>test 2 $R_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C6H5)3Hg</td>
<td>5.7</td>
<td>0.07</td>
</tr>
<tr>
<td>(C6H5)2Sn(n-C4H9)</td>
<td>2.7</td>
<td>0.97</td>
</tr>
<tr>
<td>(C6H5)3Sb</td>
<td>2.7</td>
<td>1.03</td>
</tr>
<tr>
<td>(C6H5)3Bi</td>
<td>3.0</td>
<td>1.03</td>
</tr>
<tr>
<td>(C6H5)2Te</td>
<td>3.0</td>
<td>1.07</td>
</tr>
<tr>
<td>C6H5I</td>
<td>2.9</td>
<td>0.80</td>
</tr>
<tr>
<td>C6H5Li</td>
<td>2.9</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*aComparison of the reactions of a test (C6H5Li/C6H5M, each 0.2 M) and a control (C6H5Li 0.2 M) solution with chalcone (0.2 M) in THF at -78 °C (eq 2). The control reaction gave 69% 1,2- and 24% 1,4-product. The phenyllithium solution was commercial material (1.8 M in 75:25 ether/benzene, low halide) diluted with anhydrous THF.

$R_1 = \frac{[\text{C}_6\text{H}_5\text{M}]/[\text{C}_6\text{H}_5\text{Li}]}{[\text{n-C}_4\text{H}_9\text{I}]/[\text{n-C}_4\text{H}_9\text{Li}]}.$

$R_2 = \frac{[\text{C}_6\text{H}_5\text{M}]/[\text{C}_6\text{H}_5\text{Li}]}{[\text{n-C}_4\text{H}_9\text{I}]/[\text{n-C}_4\text{H}_9\text{Li}]}.$

The possible intermediacy of transient or even stable "ate" complexes (2) as first suggested by Wittig and Schöllkopf and has been addressed experimentally for the Li-Sn exchange without definitive results. We have undertaken a study of the mechanisms of the lithium-metalloid exchange and can report substantial evidence for an intermediate in the lithium-iodine exchange.

From published results and our own studies of PhM/TolLi exchange rates ($k_1$, $k_2$), it is clear that (with minor exceptions) $k_1 > k_2$.

![Figure 2](image2)

Figure 2. Results of test 2 as a function of HMPA concentration.

The heavier and more electronegative elements exchange most rapidly. We therefore chose the phenyl derivatives of I, Te, Sb, Bi, and Sn, which reach equilibrium at -80 °C in THF in less than 5 min, as the best candidates for more careful scrutiny as to the existence of intermediate "ate" complexes. Tests comparing the reactivity of solutions of C6H5Li and 1:1 C6H5Li/C6H5M were then carried out using these metalloids. Test 1 involved a rate comparison, test 2 a rate comparison (see Table I). Of the main group organometalloids tested only iodine reproducibly showed a significant positive result for either of the tests, although the effect (~15% reduction in rate of reaction with 1-iodobutane) was not large. We therefore chose the phenyllithium-iodobenzene system for more detailed study.

Support for our hypothesis that the rate retardation was caused by the equilibrium of eq 1 was provided by the observation of further substantial decreases in the rate of alkylation (test 2) when the concentration of iodobenzene was increased. By assuming that the reaction followed second-order kinetics and that 3 was unreactive, a reasonable fit of calculated and experimental points was achieved for $K = 5.9 \text{ L mol}^{-1}$ (see Figure 1).

Table I includes an entry for diphenylmercury, which clearly indicates that complexation occurs with phenyllithium in tetra-

![Table 1](image1)


(7) Unpublished results of I. L. Reich.

(8) It should be emphasized that although for both test 2 and test 3 the reactivity of the solution varied as C6H5Li was added, the titers for active C6H5Li [measured by (CH3)2SiCl or (CH3)2S2 quench and capillary GC analysis] was always >90% of the initial value when corrected for C6H5Li used up in the test reaction.

(9) The reaction of C6H5Li with C6H5I/M is a second-order reaction at a given concentration of phenyllithium, but the rate constant changes as the [C6H5Li] is changed. It is thus not clear whether our method of measuring the "effective" concentration of free phenyllithium from the alkylation rate represents true [C6H5Li].
hydrofuran, in contrast to early results of Wittig, Meyer, and Lange, who demonstrated both by vapor pressure osmometry and a metalation test that no interaction occurs in ether. This result prompted us to study solvent effects on the iodine system (eq 1) by running test 2 in solutions containing hexamethyldisiloxane (HMPA). The small difference between the control and C₆H₅Li/CH₃I runs in THF rapidly became very large with increasing HMPA concentration (Figure 2). In fact, the addition of HMPA to a solution of C₆H₅Li/CH₃I actually lowers its reactivity. Apparently, increases in concentration of the (presumably unreactive) complex 3 as HMPA concentration was increased more than compensated for the higher reactivity of the remaining free phenyllithium. This dramatic solvent effect can be understood in terms of the differences in solvation requirements for the two sides of eq 1. In contrast to phenyl anion, which binds tightly to lithium in a cyclic dimeric structure, the diphenyliodopropyliodonium anion probably cannot provide a good coordination site for lithium cation, and hence its formation is strongly favored by improved solvation of Li⁺.

To more carefully define the stoichiometry of the interaction between phenyllithium and iodobenzene in solutions containing HMPA, test 3 was developed. Figure 3 presents the results of this test. The reactivity of the solution decreased monotonically as iodobenzene was added. The complexation is now essentially quantitative and occurs with exact 1:1 stoichiometry. If the assumption is again made that the reaction follows second-order kinetics and that the complex is unreactive toward hexamethyldisiloxane, a value of K ≈ 1.2 × 10⁻⁷ L mol⁻¹ can be estimated. This test is not reproducible with the concentration of iodine "ate" complex (C₆H₅₂⁺Li⁺ (a 10⁻¹-2 anion). This result has direct bearing on understanding the mechanism of the met-