chloride). Thus, this procedure promises to be of considerable utility for the acceleration of a wide range of Diels-Alder reactions.[13] Limitations are imposed by the instability of some dienes and dienophiles under the reaction conditions and by the preferential occurrence of Friedel–Crafts reactions in some cases.

We gratefully acknowledge a grant from the General Chemical Division, Allied Chemical Corporation, which defrayed the cost of this investigation.

[13] Following our suggestion, Mr. Kirby Scherer of these Laboratories has used aluminum chloride in dichloromethane to effect a facile Diels–Alder reaction between anthracene and 2-cyclopentenone at room temperature; in the absence of aluminum chloride the reaction in boiling xylene requires 5–6 days.

[14] N. S. F. Fellow, 1959–60.

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## SOLID COMPLEXES OF ALKYLLLITHIUM COMPOUNDS WITH LITHIUM HALIDES[1]

*Sir:*

We wish to report the preparation of a series of relatively unreactive solid complexes of alkyllithium compounds with lithium halides. Materials so far obtained have apparent formulas $RLi \cdot nLiX$, where $n$ is from 1.4 to 6, but these compositions appear to be mixtures of a 1:1 complex $RLi \cdot LiX$ with excess lithium halide. In marked contrast to alkyllithium compounds, the complexes can safely be exposed to air, and can be handled in the laboratory with no more precautions than those used with other compounds mildly sensitive to moisture and oxygen.

The complexes are produced by carrying out the well-known coupling reaction (1) between alkyllithium compounds and alkyl halides. In a hydrocarbon solvent

$$RLi + R'X \longrightarrow LiX + RR' \qquad (1)$$

the precipitate which forms is not simply lithium halide, but rather is a complex of lithium halide with the alkyllithium compound. The proportion of alkyllithium in the resulting solid varies with the conditions under which coupling is carried out.[2]

To isolate the solid complex, the precipitate from reaction (1) is filtered, washed with pentane, and dried *in vacuo*.[3] By this method complexes have been prepared from *n*-butyllithium and lithium bromide or iodide, from ethyllithium and lithium bromide, and from cyclohexyllithium and lithium bromide. In the *n*-butyllithium–lithium bromide system, which has been studied in the greatest detail, solids have been obtained with $LiBr:C_4H_9Li$ ratios of 5, 3.3, 2.0, 1.5, and 1.4. Powder X-ray diffraction patterns for all of these compositions show both lithium bromide lines and new lines characteristic of the complex.[4] The lithium bromide lines decrease in relative intensity as the amount of alkyllithium in the solid increases, and become weaker than the "complex" lines in solids with $LiBr:C_4H_9Li$ ratios less than 2. These X-ray data indicate that the solids are probably mixtures of lithium bromide with a 1:1 complex, $C_4H_9Li \cdot LiBr$.

The alkyllithium–lithium halide complexes appear to be quite different in their reactivity and properties from the ternary complexes of aryllithium, ether and lithium halide previously reported by Talalaeva and Kocheshkov.[5] The butyllithium–lithium bromide complex is rapidly hydrolyzed by water with the liberation of butane, but the rate of reaction with oxygen appears to be quite slow. Only partial decomposition was observed when the complex was exposed to laboratory air in an open beaker for three hours. The complex is also more stable thermally than is *n*-butyllithium. The latter compound undergoes rapid decomposition at temperatures above 100°,[6] while the complex is less than 50% decomposed in one hour at 160°.

The solid complexes, when suspended in pentane or benzene, are quite unaffected by Michler's ketone (negative Gilman test[7] after 30 hours contact time). The addition of ether apparently destroys the complex, and an immediate Gilman test is obtained. Thus alkyllithium compounds can be deactivated by conversion to lithium halide complexes, and then regenerated in the form of conventional organolithium reagent solutions upon addition of ether.

No evidence has yet been obtained concerning the structure of the complexes. Two limiting ionic structures, $Li^+[RLiX]^-$ and $[Li_2R]^+X^-$, could be considered, along with an intermediate electron-deficient polymeric structure. The structures of the complexes are under investigation, along with further reactions and alternate methods of preparation.

[1] This research was supported by the United States Atomic Energy Commission under contract No. AT(11-1)-64, Project No. 18.

[2] The coupling reaction may not be necessary for the synthesis of the complex, but may only provide a convenient method for slow generation of lithium halide in a solution of an alkyllithium compound.

[3] Preparations of both alkyllithium compounds and complexes were carried out in a drybox in an atmosphere of dry argon.

[4] d spacings in Å.: 16.3 (s); 8.8 (m); 5.7 (w); 4.40 (w); 4.07 (w); 3 87 (s); 3.30 (s); 2.89 (s); 2.55 (w); 2.43 (w); 2.20 (m); 1.89 (m).

[5] T. V. Talalaeva and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, **104**, 260 (1955).

[6] D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955); K. Ziegler and H. G. Gellert, *Ann.*, **567**, 179 (1950).

[7] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

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## 4-PHOSPHORINANONES

*Sir:*

Several recent papers attest to the lively interest in heterocyclic compounds containing only carbon and phosphorus in five-membered[1] and six-membered rings.[2]

We wish to report the preparation of a new class of six-membered carbon-phosphorus heterocyclic compounds, the 4-phosphorinanones (I), whose ring-carbonyl group affords an entry into an otherwise difficultly accessible area of organophosphorus chemistry.

[1] E. Howard and R. E. Donadio, Dissertation Abstracts XX, No. 2, p. 495, (1959), University Microfilms, Inc.; F. C. Leavitt, T. A. Manuel and F. Johnson, THIS JOURNAL, **81**, 3164 (1959); E. H. Braye and W. Hubel, *Chem. and Ind.*, 1250 (1959), I. G. M. Campbell and J. K. Way, *Proc. Chem. Soc.*, 231 (1959); F. G. Mann, I. T. Millar and H. R. Watson, *J. Chem. Soc.*, 2516 (1958).

[2] R. C. Hinton and F. G. Mann, *ibid.*, 2835 (1959).