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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RECEIVED JULY 7, 1960

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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RECEIVED JUNE 17, 1960

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.

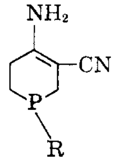
[1] E. Howard and R. E. Donadio, Dissertation Abstracts XX, No. 2, p. 495, (1959), University Microfilms, Inc.; F. C. Leavitt, T. A. Manuel and F. Johnson, THIS JOURNAL, **81**, 3164 (1959); E. H. Braye and W. Hubel, *Chem. and Ind.*, 1250 (1959), I. G. M. Campbell and J. K. Way, *Proc. Chem. Soc.*,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

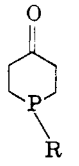
The procedure consisted of cyclizing bis-(2-cyanoethyl)-phosphines (II) to the corresponding 4-amino-1,2,5,6-tetrahydrophosphorin-3-carbonitriles (III) using sodium *t*-butoxide,[3] followed by hydrolysis and decarboxylation to the 4-phosphorinanones in refluxing 6 *N* hydrochloric acid. We also prepared an arsenic carbonitrile (IV) using the same condensing agent.

$(NCCH_2CH_2)_2PR$

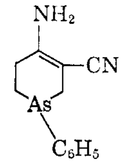
IIa, R = C_2H_5
b, R = C_6H_5



IIIa, R = C_2H_5
b, R = C_6H_5



Ia, R = C_2H_5
b, R = C_6H_5



IV

The infrared spectra of the three carbonitriles showed them to have predominantly the enamine structure, as does their carbocyclic analog, 2-amino-2-aminocyclopentene-1-carbonitrile.[4] They resinified upon heating, like 3-cyano-1-methyl-4-piperidone.[5]

The 4-phosphorinanones, I, were stable to distillation. They formed semicarbazones and methyl iodide salts in the manner normal for ketones and tertiary phosphines.

3,3'-(Phenylphosphinidene)-dipropionitrile[6] (IIb), heated with one equivalent of sodium *t*-butoxide for 3 hours in refluxing toluene, gave 4-amino-1,2,5,6-tetrahydro-1-phenylphosphorin-3-carbonitrile (IIIb) in 80% yield; m.p. 135–138°. After chromatography on alumina, the m.p. was 139.5–140°. Calcd. for $C_{12}H_{13}N_2P$: C, 66.66; H, 6.06; N, 12.96; P, 14.33; mol. wt., 216. Found: C, 66.41; H, 6.31; N, 12.81; P, 14.29; mol. wt., 218. Infrared bands at 2170 cm.$^{-1}$ (β-amino unsaturated nitrile), 3400, 3320 and 1645 cm.$^{-1}$ ($-NH_2$ group) and 1605 cm.$^{-1}$ (olefin). Hydrolysis in refluxing 6 *N* hydrochloric acid for 10 hours gave 1-phenyl-4-phosphorinanone (Ib) in 21% yield: b.p. 185–190° (1 mm.): $n^{24}D$ 1.6051 (supercooled): m.p. 43–44°. Calcd. for $C_{11}H_{13}OP$: C, 68.74: H, 6.82; P, 16.12. Found: C, 68.34; H, 6.84; P, 16.100. Infrared band at 1695 cm.$^{-1}$; m.p. of semicarbazone[7] (93% yield), 155.5–156.5°; m.p. of 1-methyl-4-oxo-1-phenyl-phosphorinanium iodide[7] 155–156°.

3,3'-(Ethylphosphinidene)-dipropionitrile[8] (IIa) gave 4-amino-1-ethyl-1,2,5,6-tetrahydrophosphorin-3-carbonitrile (IIIa) in 83% yield; m.p. 68–71°. After chromatography, the m.p. was 74.5–75°. Calcd. for $C_8H_{13}N_2P$: C, 57.13; H, 7.79; N, 16.66; P, 18.42; mol. wt., 168. Found: V, 57.14; H, 7.80; N, 16.60; P, 18.49; mol. wt., 163. Infrared bands at 3450, 3360, 2175, 1647 and 1605 cm.$^{-1}$. Hydrolysis gave 1-ethyl-4-phosphorinanone (Ia) in 23% yield; b.p. 92° (7 mm.), $n^{25}D$ 1.5180. Calcd. for $C_7H_{13}OP$: C, 58.32; H, 9.10; P, 21.49. Found: C, 58.09; H, 9.16; P, 21.25. Infrared band at 1715 cm.$^{-1}$; m.p. of semicarbazone,[7] 167–169°; m. p. of methyl iodide salt,[7] 213–214°.

3,3'-(Phenylarsylene)-dipropionitrile[9] gave 4 amino-1,2,5,6-tetrahydro-1-phenylarsenin-3-carbonitrile (IVb); m.p. 65–67°. Calcd. for $C_{12}H_{13}N_2As$: C, 55.40; H, 5.04; N, 10.77; As, 28.20; mol. wt., 260. Found: C, 55.40; H, 5.04; N, 10.58; As, 28.70: mol. wt., 277. Infrared bands at 3480, 3380, 2180, 1643 and 1605 cm.$^{-1}$.

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[3] Q. E. Thompson, THIS JOURNAL, **80**, 5483 (1958).

[4] C. F. Hammer and R. A. Hines, *ibid.*, **77**, 3649 (1955).

[5] A. H. Cook and R. J. Reed, *J. Chem. Soc.*, 399 (1945).

[6] M. M. Rauhut, *et al.*, THIS JOURNAL, **81**, 1103 (1959).

[7] Analysis was satisfactory.

[8] M. Grayson, P. T. Keough and G. A. Johnson, THIS JOURNAL, **81**, 4803 (1959).

[9] R. C. Cookson and F. G. Mann, *J. Chem. Soc.*, 618 (1947).

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RECEIVED JULY 8, 1960

REACTIONS OF ALKYL- AND ACYL-COBALT CARBONYLS WITH TRIPHENYLPHOSPHINE

Sir:

The preparation and isolation of rather unstable alkyl- and acyl-cobalt carbonyls have been reported.[1,2] It has now been found that stable derivatives can be formed from these compounds by reaction with triphenylphosphine.

Thus, acetylcobalt tetracarbonyl reacts with triphenylphosphine in ether at 0° to evolve CO. Addition of *n*-pentane and chilling yields acetylcobalt tricarbonyl triphenylphosphine as a yellow, crystalline compound, m.p. 123° (dec.). *Anal.* Calcd.: C, 61.6; H, 4.05. Found: C, 61.6; H, 4.44. Similarly, 3-butenoylcobalt tetracarbonyl yields 3-butenoylcobalt tricarbonyl triphenylphosphine, m.p. 82° (dec.). *Anal.* Calcd.: C, 63.3; H, 4.25; Co, 12.4. Found: C, 63.8; H, 4.63; Co, 11.7. The corresponding propionyl (m.p. 98–100° (dec.). *Anal.* Calcd.: C, 62.4; H, 4.36. Found: C, 62.8; H, 4.42) and isobutyryl (m.p. 101° (dec.). *Anal.* Calcd.: C, 63.0; H, 4.66. Found: C, 63.5; H, 4.78) compounds were prepared in the same manner. These compounds are stable at room temperature; the solids can be handled for short periods of time in air, but solutions oxidize rather rapidly. Proton magnetic resonance spectra are in accord with the assigned structures. All the compounds have a peak at 5.9–6.0μ in the infrared which we attribute to the acylcarbonyl group, the previously reported[1] 5.8-μ peak being shifted 0.1–0.2μ to longer wave length by the triphenylphosphine. The coördinated carbonyl bands at 5μ are shifted also by about the same amount. It is interesting that the use of a large excess of triphenylphosphine leads to the replacement of only one CO under these conditions. A limited amount of work indicates that triphenyl phosphite reacts analogously.

Several methods have been used to prepare these complexes, and in every case the reactions are in accord with the recently described chemistry of these compounds.[1,2] Thus, in the reaction of $RCOCo(CO)_4$, prepared by the acylation of $NaCo(CO)_4$ with acid halides or with alkyl halides and CO, one mole of CO per cobalt is evolved: $RCOCo(CO)_4 + P(C_6H_5)_3 \rightarrow RCOCo(CO)_3P(C_6H_5)_3 + CO$. If $RCo(CO)_4$ is used, however, no CO is evolved, in agreement with our indications that this is in equilibrium with $RCOCo(CO)_3$.

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[1] R. F. Heck and D. S. Breslow, *Chem. & Ind.* (*London*), 467 (1960).

[2] R. F. Heck and D. S. Breslow, THIS JOURNAL, **82**, 750 (1960).