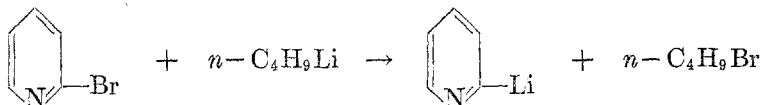


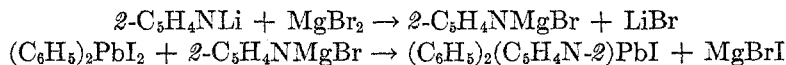
SOME 2-PYRIDYLMETALLIC COMPOUNDS

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The availability of 2-pyridyllithium (1) by the halogen-metal interconversion reaction expands the possibilities to other 2-pyridyl types.



In a reaction between diphenyllead diiodide and 2-pyridyllithium, a mixture of organolead compounds was obtained. This mixture may be due to both disproportionation or redistribution (2) and to metal-metal interconversion reactions. Since metal-metal interconversion occurs to a lesser extent with RMgX than with RLi compounds, the 2-pyridyllithium was converted to 2-pyridylmagnesium bromide with magnesium bromide (3). This Grignard reagent then reacted smoothly with diphenyllead diiodide to give diphenyl-2-pyridyllead iodide in 63% yield.



The diphenyl-2-pyridyllead iodide reacted with phenylmagnesium bromide to give triphenyl-2-pyridyllead. Interestingly enough, the 2-pyridylmagnesium bromide appeared not to react appreciably with triphenyllead iodide. Also, no metal-metal interconversion occurred at -50° between triphenyl-2-pyridyllead and *n*-butyllithium.

The reactivity of 2-pyridyllithium relative to that of phenyllithium was of interest to other studies. One of the reagents used earlier (4) for some rate studies was benzonitrile. Its reaction rate with 2-pyridyllithium was, however, too rapid. Accordingly, *p*-methoxybenzonitrile was used because of its decidedly lesser activity. It was found that 2-pyridyllithium reacts much less rapidly with *p*-methoxybenzonitrile than does phenyllithium. Interestingly, in the presence of benzene, the reaction rate with the nitrile is accelerated, probably as a result of a diluent effect by the benzene on the coordination tendencies between the RLi compound and the ethyl ether. The high yield (83-86%) of product, 2-pyridyl *p*-methoxyphenyl ketone, shows that the interconversion reaction between 2-bromopyridine and *n*-butyllithium is very satisfactory and that the lower yields of some products from 2-pyridyllithium are probably due to secondary transformations.

In addition to the formation of several 2-pyridylmetallic types, it was shown that 2-pyridyllithium adds to quinoline at -20° to give 2-pyridyl-2'-quinoline.

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It now appears that the best procedure for the preparation of 2-pyridylmagnesium halides is the interconversion reaction of 2-pyridyllithium with magnesium bromide or iodide. Other workers (5) prepared 2-pyridylmagnesium bromide in yields of 40–55% and less by a modification of the "entrainment" method of Grignard (6).

EXPERIMENTAL

Diphenyl-2-pyridyllead iodide. A solution of 14.5 g. (0.092 mole) of 2-bromopyridine in 50 cc. of ether was added over a three-minute period to 0.092 mole of *n*-butyllithium in 200 cc. of ether cooled to -20° . After seven minutes, a 0.092-mole preparation of magnesium bromide etherate (3) was added; a precipitate formed on the addition of each drop and the solution assumed a wine-red color. Then, after 15 minutes, a solution of 18.6 g. (0.03 mole) of diphenyllead diiodide (7) in 50 cc. of dry benzene was added; the mixture was stirred at -15° for five minutes, allowed to come to room temperature over a period of 90 minutes, and then hydrolyzed by pouring upon an iced ammonium chloride solution. Filtration gave 3.5 g. of an ether-insoluble residue, from which was obtained 2 g. of tetraphenyllead (mixed m.p.); the remainder was apparently lead iodide.

The ether layer yielded 8.4 g. of a solid which after successive recrystallizations from methanol and from a mixture of chloroform and petroleum ether gave yellow crystals, melting at $137-140^{\circ}$ and containing iodine.

Anal. Calc'd for $C_{17}H_{14}INPb$: N, 2.47; Pb, 36.6.

Found: N, 2.59; Pb, 36.8.

From another preparation, a 32% yield of diphenyl-2-pyridyllead iodide was obtained. In a third experiment in which the 2-pyridylmagnesium bromide was added to the diphenyllead diiodide in 100 cc. of benzene, the yield was 63%. A 62% yield was obtained in a fourth preparation in which the solid diphenyllead diiodide was added to the solution of 2-pyridylmagnesium bromide. An unresolved mixture of organolead compounds was obtained from a reaction between 2-pyridyllithium and diphenyllead diiodide.

Triphenyl-2-pyridyllead. A mildly exothermic reaction occurred on the addition of 0.01 mole of phenylmagnesium bromide to a suspension of 5.66 g. (0.01 mole) of diphenyl-2-pyridyllead iodide in 50 cc. of ether, the color changing progressively from pink to yellow to brown. Subsequent to hydrolysis by ammonium chloride solution, there was obtained 6.2 g. of a solid which contained some biphenyl. A hot methanolic extract of the solid gave crystals on cooling; the residue was then dissolved in hot chloroform to which was added, after cooling, petroleum ether (b.p. $28-38^{\circ}$) to give additional crystals. The total yield of product, melting with decomposition at 220° , was 3.5 g. (67.1%).

Anal. Calc'd for $C_{23}H_{19}NPb$: N, 2.71; Pb, 40.14.

Found: N, 2.67; Pb, 39.80.

From an experiment carried out to obtain the same product by the reaction of triphenyllead iodide and 2-pyridylmagnesium bromide, a 77% recovery of the triphenyllead iodide was effected.

There was no apparent interconversion reaction between triphenyl-2-pyridyllead and *n*-butyllithium at -50° , nor between tetraphenyllead and 2-pyridyllithium.

Tri-2-pyridylarsenic trihydrochloride. To an ether solution of 2-pyridyllithium, prepared from 13.3 g. (0.084 mole) of 2-bromopyridine, and cooled to -20° , was added 3.26 g. (0.018 mole) of freshly distilled arsenic trichloride in 20 cc. of ether. A precipitate formed in the reddish-brown solution on the addition of each drop. Subsequent to hydrolysis, the addition of hydrogen chloride to the dried ether solution gave 3.5 g. (46%) of the hygroscopic hydrochloride.

Anal. Calc'd for $C_{15}H_{15}AsCl_3N_3$: Cl, 25.44. Found: Cl, 24.98.

The addition of ammonium hydroxide to an aqueous solution of the hydrochloride gave a crystalline precipitate, which melted at $80-83^{\circ}$ after crystallization from dilute ethanol and which appears to be the dihydrate.

Anal. Calc'd for $C_{15}H_{12}AsN_3 \cdot 2H_2O$: N, 12.19. Found: N, 12.0.

The non-hydrated product was obtained from a second preparation and melted at 76–78°.

Anal. Calc'd for $C_{15}H_{12}AsN_3$: N, 13.60. Found: N, 13.62.

Di-2-pyridylmercury. A solution of 2-pyridyllithium, prepared from 0.071 mole of 2-bromopyridine and cooled to -20° , was added to a suspension of 19.3 g. (0.071 mole) of mercuric chloride in 100 cc. of ether cooled to -20° . A heavy, white precipitate formed on the addition of the RLi compound. After hydrolysis, the solid was extracted with chloroform to give 3 g. of colorless needles which melted at 198–200°. This product contained no halogen and gave a satisfactory analysis for di-2-pyridylmercury.

Anal. Calc'd for $C_{10}H_8HgN_2$: N, 7.85. Found: N, 7.94.

2-Pyridyllithium with benzonitrile and with p-methoxybenzonitrile. By means of Color Test I (8) with Michler's ketone, it was shown that reaction was complete in ten minutes when 10.8 g. (0.105 mole) of benzonitrile in 20 cc. of ether was added rapidly to 2-pyridyllithium, prepared from 0.1 mole of 2-bromopyridine in a total volume of 250 cc. of ether cooled to -20° . After hydrolysis there was obtained a 43% yield of 2-pyridyl phenyl ketone which was characterized by the preparation of the picrate (9). The same yield was obtained from a second preparation.

Under corresponding conditions, 11 g. (0.08 mole) of *p*-methoxybenzonitrile in 50 cc. of dry benzene (but not ether in this case) was added to 2-pyridyllithium, prepared from 0.08 mole of 2-bromopyridine in a total volume of 225 cc. of ether cooled to -20° . The color test became negative at the end of one hour. Hydrolysis of approximately 75% of the reaction mixture yielded 11 g. (ca. 86%) of 2-pyridyl *p*-methoxyphenyl ketone which melted at 97–99° (picrate, m.p. 183–185°). Wolfenstein and Hartwich (10) report the ketone, m.p. 93° and the picrate, m.p. 176°. However, there is probably a typographical error for they also report the melting point of 3-pyridyl *p*-methoxyphenyl ketone as 99° and the picrate as 185°. Apparently, the constants of the 2- and 3-isomers were interchanged. For this reason, our ketone was analyzed.

Anal. Calc'd for $C_{13}H_{11}NO_2$: N, 6.57. Found: N, 6.39.

The yield of ketone from a second experiment was 83%.

When a solution of 11 g. (0.08 mole) of *p*-methoxybenzonitrile in 50 cc. of benzene was added to 0.08 mole of phenyllithium in 160 cc. of ether cooled to -20° , Color Test I (8) became negative at the end of five minutes. The short time required for this reaction is very probably due to the benzene present. First, it was shown that the time reported earlier (4) (30 minutes) for completion of the reaction of phenyllithium and *p*-methoxybenzonitrile in ether alone could be checked. Second, it was shown that the replacement of the proportionate quantity of ether by benzene resulted in a completion of the reaction in five minutes.

2-Pyridyllithium and quinoline. To an ether solution of 2-pyridyllithium, prepared from 11.1 g. (0.07 mole) of 2-bromopyridine and cooled to -20° , was added slowly 9 g. (0.07 mole) of quinoline in 5 cc. of ether. A precipitate formed with each drop and the mixture darkened. Reaction was continued with stirring at -20° for ten minutes and then for an additional five minutes after removal of the cooling bath. After hydrolysis, 4 g. of quinoline (identified as the picrate) and 4.8 g. of 2-pyridyl-2'-quinoline (11), a 33% yield based on the bromopyridine, were obtained.

SUMMARY

2-Pyridyllithium can be formed in very good yield from 2-bromopyridine and *n*-butyllithium. It has been used to prepare some 2-pyridylmetallic types. The hitherto difficultly obtainable 2-pyridylmagnesium bromide is readily prepared by interaction of 2-pyridyllithium with magnesium bromide. Rate studies show that benzene, as a partial solvent, has an accelerating effect on the velocity of reaction between 2-pyridyllithium or phenyllithium and *p*-methoxybenzonitrile. 2-Pyridyllithium adds to quinoline at -20° to give 2-pyridyl-2'-quinoline.

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