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ORGANOMETALLIC π-COMPLEXES
XII*. THE METALATION OF BENZENE AND FERROCENE BY n-BUTYLLITHIUM–N,N,N',N'-TETRAMETHYLETHYLENEDIAMINE**

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INTRODUCTION

The reaction of an organic compound containing a relatively acidic hydrogen atom (R–H) and an organolithium reagent (R'–Li) is usually referred to as the hydrogen–lithium interchange, or "metalation" reaction[2].

$$\text{R–H} + \text{R'–Li} \xrightarrow{\text{solvent}} \text{R–Li} + \text{R'–H}$$

The reaction is of considerable synthetic utility in instances where R–H is sufficiently reactive, since the resulting new organolithium reagent (R'–Li) can often be used in a wide variety of subsequent reactions. The reaction has further virtue in that the by-product (R'–H) is usually a gaseous hydrocarbon which does not interfere in subsequent reactions.

Unfortunately, however, the scope of this reaction has been limited to "relatively acidic" hydrocarbons[3], *i.e.*, those having pK_A values less than approximately 34. Aromatic hydrocarbons, in particular, undergo this reaction sluggishly or not at all. For example, the reaction of benzene and organolithium compounds in hexane or ethyl ether produces little or no benzoic acid when the reaction mixture is carbonated and then hydrolyzed[4,5]. An excellent review of the hydrogen–lithium interchange (metalation) reaction covering the literature until 1954 has been prepared by Gilman and Morton[2].

Since 1954, Gilman and co-workers, as well as others, have shown that the use of mixed solvent systems (ethyl ether/tetrahydrofuran) often enhances the conversion to products in the metalation reaction in comparison to the use of ethyl ether alone. In general, the organolithium reagents have been prepared in ethyl ether and the subsequent metalation reaction of R–H has been carried out in tetrahydrofuran. In this manner, improved syntheses of lithiated derivatives of dibenzofuran[6,7], dibenzothiophene[7], naphthalene[7], diphenyl ether[8], triphenylmethane[9], toluene[9], and ferrocene[10] have been developed.

The procedure has a major drawback, however, in that the organolithium reagents used as metalating agents are relatively unstable in the presence of tetra-

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* Part XI; see ref. 1.

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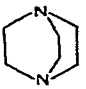
hydrofuran[11]. This difficulty can be overcome to some extent by using a large excess of the alkyllithium reagent (R′–Li), but such an excess often constitutes a problem in subsequent reactions. The excess metalating agent (R′–Li) undergoes essentially the same reactions as the newly formed organolithium reagent (R–Li).

A discovery of potentially far-reaching importance concerning the metalation reaction has recently been reported by Eberhardt and Butte[12] and by Langer[13]. These investigators found that diamines such as N,N,N′,N′-tetramethylethylenediamine (TMEDA) (I) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (II) form stable coordination complexes with various organolithium reagents, and that these complexes are considerably more reactive in the metalation reaction than are the organolithium reagents alone. It was noted, for example, that benzene underwent facile metalation using n-butyllithium–TMEDA; carbonation followed by hydrolysis or reaction with phosphorus trichloride afforded excellent yields of benzoic acid and triphenylphosphine, respectively[12,13]. When toluene was treated with n-butyllithium–DABCO and benzophenone was subsequently added to the reaction mixture, hydrolysis produced an 85% yield of benzyldiphenylcarbinol[12]. The yields of derivatized products indicate that phenyllithium and benzyllithium must have been formed in high yields in the metalation step.

$(CH_3)_2N—CH_2CH_2—N(CH_3)_2$

(I)



(II)

It should be mentioned that organolithium–diamine complexes are highly active catalysts for the telomerization of ethylene, and it is this aspect of the chemistry of these complexes that this received the greatest attention up to the present time[12,13].

The apparent ease of formation of organolithium–diamine reagents from hydrocarbons such as benzene has prompted us to undertake a research program concerned with (1) expanding the scope of the metalation reaction by means of organolithium–diamine reagents; (2) determining if the new organolithium–diamine reagents so produced can be generally useful in organic and organometallic syntheses. A portion of our work relating to benzene and ferrocene is reported herein. During the course of our program, some related studies were briefly described by Screttas and Eastham[14]. These workers have also found that the metalation of the aromatic hydrocarbons benzene, toluene and thiophene is made rapid and efficient by the presence of tertiary amines or diamines.

RESULTS AND DISCUSSION

Our initial studies were aimed at determining the optimum conditions for the metalation of benzene. Many experimental variables were examined, including method of addition, molar ratios of benzene, TMEDA and n-butyllithium, reaction temperature and time, etc. Some illustrative examples are presented in Table 1.

We found (Exp. 1) that optimum metalation of benzene occurs when the preformed n-butyllithium–TMEDA complex, prepared from equimolar amounts of organolithium reagent and diamine, is allowed to react with benzene at room tem-

TABLE 1

THE METALATION OF BENZENE WITH n-BUTYLLITHIUM–TMEDA AND SUBSEQUENT CARBONATION[a]

Exp. No.	*n-C_4H_9Li (mmoles)*	*TMEDA (mmoles)*	*Yield of C_6H_5COOH (%)*[b]
1	60	60	92
2	60	60	49[c]
3	240	240	95[d]
4	60	0	0
5[e]	60	60	0
6	60	60[f]	3
7	60	120	69
8	60	30	63
9	60	15	75

[a] In each run, unless otherwise noted: (1) a large molar excess of benzene was employed; (2) the reaction period prior to carbonation was 3 h; (3) the reaction temperature was 25°. [b] Yield data is normally the average of several runs under the same conditions. [c] The reaction temperature was 78° (reflux). [d] Sixty mmoles of benzene was employed; the yield is based upon benzene. [e] Tetrahydrofuran (40 ml) was used as a co-solvent with hexane. [f] Dimethoxyethane was used in place of TMEDA.

perature for a period of 3 h. The reaction mixture was carbonated and then hydrolyzed using a minimum amount of water, in order to facilitate isolation of a maximum amount of benzoic acid. In six such experiments under these conditions, the yield of benzoic acid varied from 78 to 98 %, with an average yield of 92 %*. When the reaction mixture was refluxed for a 3-h period, the yield of benzoic acid (and presumably phenyllithium) decreased significantly (Exp. 2), due possibly to subsequent attack of phenyllithium on the diamine. A number of metalations (Exp. 7–9) were conducted in which molar excesses of either n-butyllithium or TMEDA were employed. In all such cases we studied, the yield of benzoic acid was somewhat lower than the yield obtained using equimolar amounts of these reagents. Several attempts (Exp. 3) were made to effect the dimetalation of benzene by utilizing a large molar excess of n-butyllithium–TMEDA in relation to benzene. In no case following carbonation and hydrolysis could any phthalic acids be detected, although the yield of benzoic acid was uniformly high.

Since tetrahydrofuran has been shown to enhance the metalation reaction in earlier studies[6–10], its effect under the present experimental conditions was of interest. As shown by Exp. 5, the presence of tetrahydrofuran appeared to be very deleterious, and no benzoic acid could be isolated following carbonation and hydrolysis. In view of the known ability of oxygen to coordinate with the lithium ion, several other attempts were made to employ diethers such as dimethoxyethane in the metalation reaction in conjunction with n-butyllithium. As shown by Exp. 6, only very poor yields of benzoic acid resulted. Moreover, the addition of n-butyllithium to a mixture of hexane and dimethoxyethane proved to be strongly exothermic and difficult to control, even at low temperatures. Finally, several control experiments (Exp. 4)

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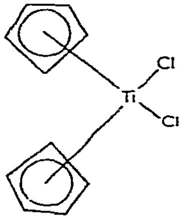
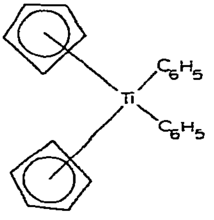
* The characterization of metalation products by the carbonation method is not always a reliable quantitative method. The actual yields of phenyllithium and 1,1'-ferrocenylenedilithium in the present studies may therefore be higher than the yields of benzoic acid and 1,1'-ferrocenedicarboxylic acid respectively indicate.

confirmed earlier findings[5] that benzene is not metalated by n-butyllithium alone.

Employing the optimum conditions for the metalation of benzene as indicated by the carbonation studies, we set out to determine if the same high yields of phenylated products could be obtained in other organic and organometallic syntheses. The addition of equimolar amounts of either benzophenone or triphenylchlorosilane to phenyllithium formed by the metalation process resulted in triphenylcarbinol and tetraphenylsilane in yields of 93 % and 97 %, respectively. The reaction of equimolar amounts of phenyllithium and mercuric chloride produced a 93 % yield of crude phenylmercuric chloride, while a 2 : 1 ratio of phenyllithium to mercuric chloride afforded the expected product, diphenylmercury, in a yield of 89 %. The potential utility of phenyllithium formed by the metalation route was further indicated by a reaction between this reagent and titanocene dichloride (III). The product, di(π-cyclopentadienyl)di(σ-phenyl)titanium [di(σ-phenyl)titanocene] (IV) was obtained in 96 % yield.



(III)



(IV)

We next turned our attention to the dimetalation of ferrocene. Very early in the development of ferrocene chemistry, it was reported that this organo-iron compound could be lithiated in rather low yield by n-butyllithium in ethyl ether solution[15,16]. Subsequent extensions of mixed solvent system studies (ethyl ether/tetrahydrofuran) to ferrocene afforded considerably better overall yields of lithiated ferrocenes, although mixtures of both mono- and dilithiated ferrocenes were still invariably obtained[10]. Such mixtures often result in separation problems in subsequent conversions of the lithiated intermediates. Nesmeyanov and coworkers[17,18] later reported that reasonably good yields of 1,1′-ferrocenylenedisodium resulted from the reaction of ferrocene with either amyl- or phenylsodium, but the reliability of this method seems questionable on the basis of additional studies by Seyferth and coworkers[19].

Some representative examples of our studies concerning the lithiation of ferrocene by n-butyllithium–TMEDA followed by carbonation and hydrolysis are summarized in Table 2. As illustrated by Exp. 1, the optimum conditions for the dilithiation of ferrocene utilized a slightly greater than 2 : 1 molar ratio of n-butyllithium and diamine to ferrocene, and a reaction period of 6 h, the reaction being run at room temperature. Under these conditions, five separate experiments produced 1,1′-ferrocenedicarboxylic acid (VI) in yields ranging from 88 to 98 %, the average yield being 94 %. In analogy to the benzene studies, yields of the diacid (VI) were invariably lower when the metalation was attempted under reflux conditions (Exp. 3). When *exactly* a 2 : 1 molar ratio of metalating agent to ferrocene was employed, either at room temperature or at reflux (Exp. 2, 4), the yields of diacid (VI) were also lower, indicating incomplete conversion to 1,1′-ferrocenylenedilithium (V).

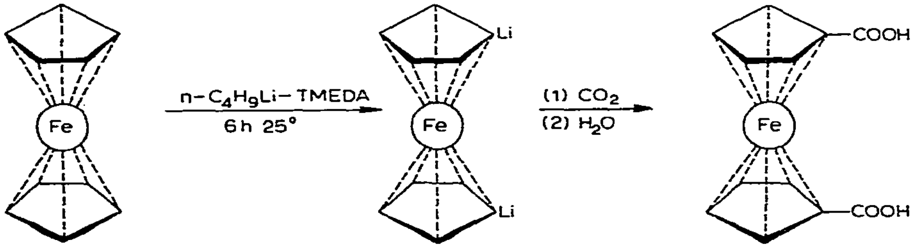
TABLE 2

THE METALATION OF FERROCENE WITH n-BUTYLLITHIUM–TMEDA AND SUBSEQUENT CARBONATION[a]

Exp. No.	*Ferrocene (mmoles)*	*n-C_4H_9Li (mmoles)*	*TMEDA (mmoles)*	*Solvent*	*Reaction temp. (°C)*	*Yield of $Fe(C_5H_4COOH)_2$ (%)[b]*
1	30	74	74	hexane	25	94
2	30	60	60	hexane	25	65
3	30	74	74	hexane	78	58
4	30	60	60	hexane	68	50
5	30	74	74	ethyl ether	25	63[c]
6	30	74	74	ethyl ether	38	60
7	60	60	60	hexane	25	36[d]

[a] The reaction period prior to carbonation was 6 h for Exps. 1–6, and 3 h for Exp. 7. [b] Yield data is normally the average of several runs under the same conditions. [c] A 3 % yield of ferrocenoic acid and a 25 % recovery of ferrocene was noted. [d] Yields of ferrocenoic acid averaged 11 %.

The use of ethyl ether instead of hexane as the solvent for metalation of ferrocene likewise resulted in lower conversion to the dilithium reagent (V), as evidenced by carbonation studies (Exp. 5, 6). This result was surprising, since ethers are normally preferred solvents over hydrocarbons for the metalation reaction[20].



(V) (VI)

Several attempts to exclusively monolithiate ferrocene in high yield were not successful using the n-butyllithium–TMEDA procedure (Exp. 7). The reaction of equimolar amounts of n-butyllithium, TMEDA and ferrocene in hexane solution followed by carbonation and hydrolysis invariably produced the diacid (VI) in 30–36 % yield, while only 9–13 % of ferrocenoic acid could be obtained. The dilithium reagent (V) thus appears to be appreciably stable and in equilibrium with ferrocenyllithium under the present conditions, and a direct, high-yield route to the latter reagent still needs to be devised to complement the dimetalation procedure described above.

Several additional reactions of dilithium reagent (V) were investigated in conjunction with the present study. Reactions with either benzophenone or pyridine, for example, produced 1,1′-bis(diphenylhydroxymethyl)ferrocene and 1,1′-di(2-pyridyl)ferrocene in yields of 80 % and 30 %, respectively; it should be noted that the latter compound was obtained in only 3 % yield in two earlier studies[21,22]. The potential utility of the dilithium reagent (V) prepared by the n-butyllithium–TMEDA procedure is also illustrated by the facile conversion of this reagent to 1,1-dihaloferrocenes[23] and to polyferrocenylenes[24]. Details of these and other studies will be reported in subsequent papers in this series.

During the course of our studies, Peterson and Hays[25] reported that the methyl group of methyldiphenylphosphine can be metalated using organolithium reagents in a variety of solvents. They found, for example, that the rate of metalation of methyldiphenylphosphine by n-butyllithium was considerably faster in ethyl ether than in pentane. Under identical reaction conditions (48 h), the phosphine was metalated to the extent of 21 % by n-butyllithium in ethyl ether, whereas the phosphine was *inert* to n-butyllithium in the hydrocarbon solvent. It was therefore of interest to study briefly this reaction under our metalation conditions. When the procedure of Peterson and Hays was repeated using n-butyllithium–TMEDA as the metalating agent in hexane solution, workup of the reaction mixture according to the method outlined by these authors indicated that the phosphine had been converted into (diphenylphosphino)methyllithium in 54 % yield. The enhanced reactivity of n-butyllithium–TMEDA compared to the organolithium reagent alone in the metalation reaction is thus once again demonstrated.

The enhanced metalating ability of n-butyllithium–TMEDA may possibly result from coordination of the diamine with vacant 2*p* orbitals of the lithium ion. Such a process might conceivably polarize the carbon–lithium bond to such an extent that the butyl group becomes a considerably more powerful nucleophile than in n-butyllithium alone[12,13]. Whatever the reason, the diamine has thus far not presented complications in subsequent reactions of the newly formed organolithium compounds, and it seems clear that this new metalating agent will play an important role in extending the scope of the metalation reaction*.

EXPERIMENTAL SECTION

While conducting any experiment which requires n-butyllithium, special care must be taken to insure against the decomposition of the reagent. The n-butyllithium (22.8 % in hexane) was purchased from Alfa Inorganics, Inc. N,N,N′,N′-tetramethylethylenediamine was obtained from Matheson, Coleman and Bell (practical grade, b.p. 120–122°) and was distilled through a Vigreaux column, collecting only that fraction that distilled at 120.5°. The diamine was then stored in the dark in a tightly closed brown bottle. All solvents were of reagent grade and were distilled from sodium and stored over calcium hydride. Benzene was azeotropically distilled and was stored over sodium wire. Ferrocene was obtained from Arapahoe Chemicals, Inc., while triphenylchlorosilane was generously donated by the Dow-Corning Corp. All flasks were evacuated under reduced pressure and then refilled with nitrogen; the flushing process was repeated several times before a reaction was initiated.

The metalation of benzene with n-butyllithium–TMEDA. Formation of benzoic acid

Into a 3-necked flask, equipped with a nitrogen inlet tube, magnetic stirring

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* After this study had been completed, Dr. Langer kindly informed us that he has isolated a variety of new aryllithium–TMEDA complexes as crystalline solids. He also has pointed out that groups as weakly acidic as $N{-}CH_3$ can be metalated; in fact, the $N{-}CH_3$ group of TMEDA is metalated slowly by n-butyllithium–TMEDA at room temperature (see also ref. 13). As a preparative tool, therefore, the metalation of aromatic hydrocarbons by this reagent is limited to compounds which are of comparable or greater acidity than the $N{-}CH_3$ group of TMEDA. However, metalation by n-butyllithium–TMEDA represents a major extension of the metalation reaction to include compounds which are only very slightly more acidic than saturated hydrocarbons.

bar and condenser fitted with a mercury overpressure valve, was added 9.03 ml (60 mmoles) of TMEDA and 15 ml of anhydrous hexane. To this mixture was added via a syringe 25 ml (60 mmoles) of n-butyllithium while stirring was initiated with a magnetic stirrer. The complex was allowed to form, and after 10 min 200 ml of dry, thiophene-free benzene was added to the cloudy slurry. The pale yellow solution was stirred for 3 h at room temperature. The solution was then rapidly poured with rapid stirring onto 300 ml of anhydrous ethyl ether mixed with finely crushed dry ice. The mixture was allowed to warm to room temperature and the lithium salt was filtered and was washed with several portions of cold ethyl ether. The salt was then collected and acidified with a small amount of conc. hydrochloric acid. The benzoic acid was filtered, washed several times with cold water, and was dried and weighed (7.2 g, 98 %, m.p. 121–122°).

Alternatively, the carbonated mixture was evaporated to dryness in a stream of air, the residue was acidified with cold, dilute hydrochloric acid, and the benzoic acid was extracted with ethyl ether.

Triphenylcarbinol

To a solution of 60 mmoles of phenyllithium prepared in the above manner was added under nitrogen a solution of 10.97 g (60 mmoles) of benzophenone in 250 ml of ethyl ether. The reaction mixture was stirred for 3 h, hydrolyzed with dilute hydrochloric acid, and filtered. Triphenylcarbinol (14.5 g) was obtained in a 93 % yield and had a m.p. of 162°.

Tetraphenylsilane

To a solution of 60 mmoles of phenyllithium prepared in the above manner was added dropwise under nitrogen a solution of 17.8 g (60 mmoles) of triphenylchlorosilane in 200 ml of ethyl ether. The reaction mixture was stirred at room temperature for 2 h, then stirred at reflux for an additional 2 h. The precipitate which had formed, after washing with ethyl ether, hot water, and drying, afforded 16.50 g of tetraphenylsilane, m.p. 237–238°. The ether soluble portion was evaporated to dryness, and the residue was washed with hot water and a small amount of hexane to produce an additional 3.05 g of product, m.p. 235–237°, for a total yield of 97 %.

In a duplicate experiment in which the metalation period was extended to 18 h at room temperature, the yield of tetraphenylsilane was 87 %.

Diphenylmercury and phenylmercuric chloride

To a solution of 60 mmoles of phenyllithium prepared as described above was added a solution of 8.15 g (30 mmoles) of mercuric chloride in 250 ml of ethyl ether over a period of 1 h. Following completion of the addition, the reaction mixture was allowed to stir at room temperature for a period of 17 h, and then was refluxed for an additional hour. After cooling to room temperature, the solvent was evaporated by means of an air jet in an efficient fume hood (the product appeared somewhat oily at this point, and smelled of di-n-butylmercury). The residue was extracted twice with 100 ml portions of boiling 1 % hydrochloric acid, once with water, and was filtered. After drying the product in a vacuum oven at room temperature overnight, there remained 9.42 g (89 %) of diphenylmercury, m.p. 124–125°. A mixed m.p. determination with an authentic sample was undepressed. The product could be further purified by recrystallization from n-propyl alcohol, forming long white needles of m.p. 125.5–126°.

The addition of 60 mmoles of phenyllithium solution, prepared in the above manner, to 16.29 g (60 mmoles) of mercuric chloride in 750 ml of ethyl ether, followed by workup as described above, produced a 93% crude yield of phenylmercuric chloride. Recrystallization of the product from either n-propyl alcohol or cumene, or (more conveniently) extraction with methyl alcohol in a Soxhlet extractor, produced white platelets, m.p. 256–257° (lit.[26] 251°). The phenylmercuric chloride appeared to rapidly sublime in the m.p. tube on heating above *ca.* 250°.

Di(π-cyclopentadienyl)di(σ-phenyl)titanium[di(σ-phenyl)titanocene]

Phenyllithium (120 mmoles) was prepared in the usual manner in a 3-necked 1-liter flask equipped with a Teflon stopcock on the bottom of the flask. The phenyllithium solution was added under nitrogen over a 3 h period to a stirred suspension of titanocene dichloride (Arapahoe Chemicals, Inc., 15.0 g, 60 mmoles) in 250 ml of ethyl ether at room temperature. The reaction mixture was filtered in air, and the insoluble portion was washed with methylene chloride. The organic portions were combined and the solvent was removed on a rotary evaporater. The product was purified by dissolving it in methylene chloride, filtering any insoluble material, adding pentane until crystals began to precipitate, and filtering the crystals. Successive crops were collected in a similar manner, producing 19.2 g (96% yield) of di(π-cyclopentadienyl)di(σ-phenyl)titanium, m.p. 142–144° (dec.) [lit.[27] 146–148° (dec.)].

The proton NMR spectrum of (IV) (satd. soln. in $CDCl_3$) exhibited singlet resonances at τ 3.07 and 3.78 ppm due to the phenyl and π-cyclopentadienyl hydrogen atoms, respectively.

The dimetalation of ferrocene with n-butyllithium–TMEDA. Formation of 1,1′-ferrocenedicarboxylic acid

Into a 3-necked flask, equipped with a nitrogen inlet tube, a magnetic stirring bar and a condenser fitted with a mercury overpressure valve, was added 11.1 ml (74 mmoles) of TMEDA and 10 ml of anhydrous hexane. To this mixture was added through a syringe 30 ml (74 mmoles) of n-butyllithium in hexane solution. The n-butyllithium–TMEDA was allowed to form, and after 10 min a solution of 5.60 g (30 mmoles) of ferrocene in 250 ml of anhydrous hexane was added with rapid stirring over a period of 30 min. The reaction mixture was allowed to stir at room temperature for an additional 6 h, during which time orange crystals were observed to be formed. The reaction mixture was then poured with rapid stirring onto a mixture of finely crushed dry ice and anhydrous ethyl ether. After warming to room temperature, the mixture was filtered and the insoluble material was washed once with cold ethyl ether. This lithium salt was acidified with a small volume of conc. hydrochloric acid and the resulting acid was filtered, washed with water, and was dried.

Repeated benzene extraction of this material produced 0.125 g (1.8% yield) of ferrocenoic acid, m.p. 190–194° (dec.) [lit.[15] 195–205° (dec.)]. The benzene insoluble material after drying consisted of 8.08 g (98%) of 1,1′-ferrocenedicarboxylic acid, dec. over 240° (lit.[15] dec. over 250°). From the ether portion, about 20 mg of ferrocene was recovered.

Other experiments involving the metalation of ferrocene with n-butyllithium–TMEDA and subsequent carbonation are summarized in Table 2.

1,1-*Bis(diphenylhydroxymethyl)ferrocene*

1,1'-Ferrocenylenedilithium (30 mmoles) was prepared as described above in anhydrous hexane. A solution of 13.1 g (77 mmoles) of benzophenone in 250 ml of anhydrous hexane was added and the reaction mixture was allowed to stir for an additional 6 h at room temperature. Following hydrolysis with *ca.* 300 ml of cold water, the insoluble material was filtered and was washed with cold water and with cold hexane. There remained 13.2 g (80%) of 1,1'-bis(diphenylhydroxymethyl)-ferrocene, m.p. 179–181° (lit.[28] 179–180°). From the organic portion, 95 mg (1 % yield) of (diphenylhydroxymethyl)ferrocene, m.p. 136–138° (lit.[19] 133–136°) and 0.62 g of ferrocene were isolated by means of column chromatography on alumina.

1,1'-*Di(2-pyridyl)ferrocene*

1,1'-Ferrocenylenedilithium (30 mmoles) was prepared as described above in anhydrous hexane. Pyridine (6.47 ml, 80 mmoles), which had been freshly distilled from calcium hydride, was added slowly to the lithium reagent, and the reaction mixture was stirred at reflux for 36 h. After cooling to room temperature, 300 ml of water was added, the phases were separated, the aqueous phase was extracted with ether, and the combined organic phase and extracts was concentrated and chromatographed on alumina. The first band was eluted with ethyl ether and produced 3.25 g (58 % recovery) of ferrocene. A second band which eluted more slowly with ethyl ether was collected and afforded 0.40 g of a red solid, m.p. 164–165°. The last red band was eluted with methylene chloride and yielded 3.08 g (30 % yield) of 1,1'-dipyridylferrocene, m.p. 184–185° (lit.[22] 188–189°).

In several other runs, attempts to recrystallize the oily chromatographic product were not successful. In such cases, 1,1'-dipyridylferrocene was isolated as its dihydrochloride, m.p. 100–104° (dec.), by dissolving the chromatographed portion in ethyl ether and bubbling through dry hydrogen chloride until no additional precipitate was formed.

Metalation of diphenylmethylphosphine with n-butyllithium–TMEDA

Into a 250-ml, 1-necked flask equipped with a nitrogen inlet was introduced 18.0 ml (0.123 mole) of TMEDA, 50 ml of anhydrous hexane and 50 ml (0.123 mole) of n-butyllithium in hexane solution. To the complex was added 12.5 ml (0.063 mole) of diphenylmethylphosphine[29] under nitrogen, and the reaction mixture was stirred at room temperature for 48 h by means of a magnetic stirrer. The yellow solution was carbonated by pouring it into a dry ice/ethyl ether mixture. Treatment with sulfur and subsequent workup according to the method of Peterson and Hays[25] produced 9.3 g. (54% yield) of (carboxymethyl)diphenylphosphine sulfide, m.p. 192–195° (lit.[25] 195–198°).

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SUMMARY

A detailed study has been made concerning the metalation of benzene and ferrocene by means of n-butyllithium + N,N,N',N'-tetramethylethylenediamine in hexane and ethyl ether solution. Optimum conditions are described for the formation of phenyllithium and 1,1'-ferrocenylenedilithium, and the utility of these reagents in organic and organometallic syntheses is demonstrated by their conversion in good yield to a variety of products. The n-butyllithium–diamine complex in hexane has been shown to metalate the methyl group of methyldiphenylphosphine in 54% yield.

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