PERHALOARYL–METAL CHEMISTRY[*]

II. PENTACHLOROPHENYLLITHIUM[**]

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(Received October 18th, 1965)

Following the discoveries that pentafluorophenylmagnesium bromide[2,3] and pentafluorophenyllithium[4] are readily prepared and exhibit moderate stabilities in ethereal solutions, many research groups have utilized these reagents in developing the chemistry of highly fluorinated organic derivatives of metals and metalloids. Our initial communication in this area described briefly the ease of formation, the relatively high stabilities, and the spectra of certain pentafluorophenyl–transition metal compounds[1]. Similar studies concerning pentafluorophenyl derivatives of various transition metals have been reported recently by Stone and co-workers[5]. In addition, the formation and properties of a large number of pentafluorophenyl derivatives of non-transition metals and metalloids have now been described in the literature.

In conjunction with our general research program concerning σ-bonded organic derivatives of the transition metals, it was of interest to develop a convenient route to corresponding pentachlorophenyl–transition metal compounds. Pentachlorophenyl-magnesium chloride has recently been described in the literature[6,7] and a limited number of studies[7–9] have utilized this intermediate for the preparation of penta-chlorophenyl derivatives. The corresponding lithium reagent, pentachlorophenyl-lithium (I), has not previously been reported. Since organolithium reagents are ordinarily more reactive in many reactions than are related Grignard reagents, a facile synthesis of pentachlorophenyllithium seemed desirable.

We have found that pentachlorophenyllithium can be readily prepared by the addition of commercially available n-butyllithium in hexane to an equimolar amount of hexachlorobenzene in an ethereal solvent. When the reaction was conducted in tetra-hydrofuran, it was found desirable to maintain the reaction temperature at $-78°$ in order to obtain a satisfactory yield of (I). In ethyl ether as the solvent, reaction temperatures as high as $-10°$ could conveniently be employed.

$$C_6Cl_6 + n\text{-}C_4H_9Li \xrightarrow[\text{or THF}]{Et_2O} C_6Cl_5Li \text{ (I)} + n\text{-}C_4H_9Cl$$
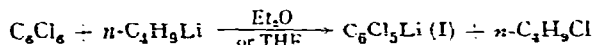
A number of reactions have been carried out in order to characterize pentachloro-phenyllithium and to examine its utility in organic and organometallic synthesis. Thus, treatment of (I) in tetrahydrofuran solution with water produced pentachloro-

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[*] For Part I, see ref. 1.

[**] Presented in part at the Second International Symposium on Organometallic Chemistry, Madison, Wisconsin (U.S.A.), Aug. 30–Sept. 3, 1965; see Abstracts of Proceedings, p. 7.

benzene in 56 % yield. 2,3,4,5,6-Pentachlorobenzhydrol was obtained in 81 % yield from the reaction of benzaldehyde and (I) in ethyl ether solution. The reaction between (I) in ethyl ether solution and benzophenone proceeded with surprising ease; diphenyl-pentachlorophenylcarbinol was obtained in 74 % yield. Carbonation of (I) prepared in either tetrahydrofuran or ethyl ether produced pentachlorobenzoic acid in yields of 56 % and 65 %, respectively.

Initial studies have shown that a large variety of pentachlorophenyl derivatives of metals and metalloids are accessible using this new organolithium reagent. For example, diphenyl(pentachlorophenyl)phosphine (60 %) and (pentachlorophenyl)-trimethylsilane (48 %) were readily formed from the reaction of the appropriate chlorophosphine or chlorosilane and (I) in ethyl ether and tetrahydrofuran solution, respectively. The reaction of (I) in ethyl ether solution with mercuric chloride has produced bis(pentachlorophenyl)mercury in higher yield (84 %) than the previously reported route using pentachlorophenylmagnesium chloride[9].

In order to further characterize pentachlorophenyllithium, the formation of several pentachlorophenyl derivatives of nickel and cobalt prepared previously by Chatt and Shaw[8] (employing pentachlorophenylmagnesium chloride) were attempted. Bis(diethylphenylphosphine)pentachlorophenylnickel chloride, $[(C_2H_5)_2(C_6H_5)P]_2Ni(C_6Cl_5)Cl$, and bis(diethylphenylphosphine)bis(pentachlorophenyl)cobalt, $[(C_2H_5)_2(C_6H_5)P]_2Co(C_6Cl_5)_2$, were formed in yields of 60 % and 33 %, respectively, when (I) in tetrahydrofuran solution was treated with either bis(diethylphenylphosphine)-nickel dichloride or -cobalt dichloride. Both reaction products were shown to be identical to products obtained earlier using the Grignard method. Preliminary studies have shown that a variety of new pentachlorophenyl–transition metal derivatives can be prepared starting with pentachlorophenyllithium and appropriate metal halides, and these results will be reported in future publications.

The principal infrared absorption peaks of the various pentachlorophenyl derivatives prepared in this study are given in the Experimental Section. Although no definite assignments can be made at this time, we have noted that all pentachloro-phenyl derivatives studied thus far exhibit moderate to strong absorption in each of the following regions: 670–698 cm⁻¹; 826–865 cm⁻¹; 1088–1125 cm⁻¹. Dessy and co-workers have previously reported that pentachlorophenylmercury derivatives exhibit a sharp, intense absorption in the range 845–855 cm⁻¹ (Ref. 9).

A preliminary study of the stability of pentachlorophenyllithium in solution has been made. The results are summarized in Table 1. In general, aliquot samples of (I) in either ethyl ether or tetrahydrofuran solution were withdrawn at various time intervals and were carbonated. From the amount of pentachlorobenzoic acid thus produced, an estimate of the concentration of pentachlorophenyllithium as a function of time and temperature was obtained. When ethyl ether was employed as the solvent, yields of (I) of approximately 80 % were noted upon completion of the addition of n-butyllithium at −10°. Even when the solution temperature was allowed to warm to 20° over a seven hour period, carbonation indicated that (I) was still present in 59 % yield.

Pentachlorophenyllithium appears to be appreciably less stable in tetrahydro-furan solution. Yields of (I) prepared in tetrahydr·furan were consistently lower than those using ethyl ether. Even at −78°, the concentration of (I) dropped off gradually over a period of forty hours. Melting point determinations indicated that the penta-

TABLE 1

STABILITY OF PENTACHLOROPHENYLLITHIUM IN ETHEREAL SOLUTION

Solvent	Reaction period (h)	Solution temp. (°C)	Yield of C_6Cl_5COOH (%)
Ethyl ether	0[a]	—10	80
	1/3	—10	82
	2	0	74
	7	20	59
Tetrahydrofuran	7	—78	46
	21	—78	47
	30	—78	36
	42	—78	34

[a] Zero time period is defined as the time at which the addition of n-butyllithium to hexachlorobenzene is completed.

chlorobenzoic acid formed in this manner became increasingly less pure when (I) was allowed to stand at —78° for more than seven hours and then carbonated. The nature of the by-products has not yet been elucidated.

The comparatively high stability of (I) in ethyl ether solution is comparable to the stability reported for pentafluorophenyllithium[3]. As in the case of the fluorine analog, this enhanced stability may be associated with stabilization of the carbanion due to the electronegative nature of the five chlorine atoms. The relative stabilities of both pentahalophenyllithium reagents are in marked contrast to the stabilities of mono-ortho-halogenated phenyllithium derivatives, which are known to eliminate lithium halide readily even at low temperatures with the formation of benzyne[10,11].

Studies are currently in progress in an attempt to detect the formation of tetrachlorobenzyne as a product of decomposition of (I). Tetrafluorobenzyne has already been postulated to be an intermediate in reactions involving pentafluorophenyllithium[3].

The facile formation of pentachlorophenyllithium from hexachlorobenzene and n-butyllithium is of additional interest, since the halogen–lithium interconversion reaction has been confined almost exclusively to organic bromides and iodides. Only a few examples of interconversions involving chlorides have been observed, and these include certain alkyl chlorides such as benzyl chloride, trityl chloride, β-chlorostyrene, phenylethynyl chloride, etc.[12]. The present result thus represents the first example of halogen–lithium interconversion involving a benzenoid aromatic chloride*.

The ease of formation, moderate stability and general reactivity of pentachlorophenyllithium as reported here should make this reagent a valuable synthetic intermediate in organic and organometallic chemistry. In addition, both hexachlorobenzene and n-butyllithium are readily available materials, and the former is presently far less expensive than corresponding highly fluorinated benzenes. A comparison of the relative stabilities and reactivities of pentachloro- and pentafluorophenyl

* Treatment of 2,4,5-triphenyl-3-chlorofuran with n-butyllithium, followed by carbonation, has been reported to produce 2,4,5-triphenyl-3-furancarboxylic acid in 14% yield. In contrast, the latter was formed in 78% yield starting with the corresponding 3-bromo derivative[13].

derivatives of metals and metalloids, especially with regard to possible steric and electronic differences, is currently under investigation in our Laboratory.

EXPERIMENTAL

Ethyl ether was purified by drying over sodium wire, followed by passage through Linde Molecular Sieve (No. 5A). Tetrahydrofuran was purified by either passage through Linde Molecular Sieve or distillation from lithium aluminum hydride. Hexachlorobenzene (Matheson, Coleman and Bell) was purified by recrystallization from benzene and subsequently from n-heptane; m.p. 228.0–228.5° (reported[14] m.p. 226–227.5°). Commercial n-butyllithium in hexane solution was obtained either from the Foote Mineral Co. or from Alfa Inorganics, Inc.

Preparation of pentachlorophenyllithium

(a) *In ethyl ether*. The reaction was carried out in a 500-ml three-necked flask equipped with a nitrogen inlet, a condenser (connected to a mercury check valve), a pressure-equalizing addition funnel, and a magnetic stirring bar. The system was evacuated and was flushed with dry, prepurified nitrogen; this process was repeated three times. With nitrogen passing through the system, hexachlorobenzene (5.69 g, 0.02 mole) was added to the flask followed by 400 ml of purified ethyl ether. The required volume of commercial n-butyllithium in hexane (containing 0.02 mole of n-butyllithium) was added to the addition funnel by means of a syringe. The contents of the flask was cooled to —10° to —15° by means of an ice–salt bath. With rapid stirring, the n-butyllithium solution was added slowly over a period of 30 to 45 min. At the end of this period, no insoluble hexachlorobenzene was visible in the flask, and the slightly opaque solution of pentachlorophenyllithium was light yellow in color.

(b) *In tetrahydrofuran*. The reaction system was similar to that described in (a), except that a low temperature alcohol thermometer was inserted into the flask. Hexachlorobenzene (5.69 g, 0.02 mole) and tetrahydrofuran (50 ml) were added to the flask under nitrogen, and the contents were cooled to approximately —78° by means of an acetone–dry ice bath. The required volume of commercial n-butyllithium solution (containing 0.02 mole of n-butyllithium) was transferred to the addition funnel by means of a syringe. The n-butyllithium solution was then added dropwise with stirring to the contents of the flask, so as to maintain the reaction at —78°. Following the addition, the reaction mixture stirred for an additional 20 min at —78°, after which time very little solid hexachlorobenzene was visible, and the reaction mixture had assumed a light orange-brown color.

Diphenyl(pentachlorophenyl)phosphine

Diphenylchlorophosphine (4.42 g, 0.02 mole, Aldrich Chemicals Co.) was added via an addition funnel over a period of 30 min to pentachlorophenyllithium (0.02 mole) prepared in ethyl ether solution. The reaction mixture was maintained with stirring at —10° during the addition, and then allowed to warm to room temperature with stirring over a period of 24 h. The reaction mixture was hydrolyzed with 100 ml of water and the layers were separated. The ether layer was washed with 100 ml of 1 % sodium hydroxide solution, twice with 100 ml portions of water, and was dried over anhyd. sodium sulfate. The ether was evaporated yielding 7.43 g of a pale-yellow

solid. This was recrystallized from hexane to produce 5.24 g (60 % yield) of white crystals, m.p. 126–127°. An analytical sample, m.p. 131.8–132.4°, was prepared by recrystallization from ethanol. (Found: C, 49.77; H, 2.45; Cl, 40.68; P, 7.04. $C_{18}H_{10}Cl_5P$ calcd.: C, 49.73; H, 2.32; Cl, 40.82; P, 7.13 %.)

The IR spectrum (CS_2 soln.): 693, 742, 864, 1094, 1284, 3077 cm⁻¹. The NMR spectrum (CCl_4 soln.): absorption between 2.65 and 2.72 τ, with a sharp resonance at 2.72 τ.

Diphenyl(pentachlorophenyl)carbinol

Benzophenone (3.64 g, 0.02 mole) in 25 ml of ethyl ether was added to penta-chlorophenyllithium (0.02 mole) in ethyl ether at −10° over a period of 30 min. The mixture was stirred and allowed to warm to room temperature over a period of 2 h. After the addition of 100 ml of water, the layers were separated, the ether layer was washed twice with water, and was dried over anhyd. sodium sulfate. Evaporation of the ether yielded 7.11 g of white solid. This was recrystallized from hexane to give 6.15 g (71 % yield) of pale-yellow crystals, m.p. 150–152°. An analytical sample, m.p. 152.5–153.8°, was obtained in the form of white crystals by recrystallization from hexane. (Found: C.52.61; H, 2.26; Cl, 40.92. $C_{19}H_{11}Cl_5O$ calcd.: C, 52.76; H, 2.54; Cl, 40.99%.)

The IR spectrum (CS_2 soln.): 697, 769, 828, 1071, 1323, 1344, 3077, 3584 cm⁻¹. The NMR spectrum (CS_2 soln.) exhibited a resonance due to the hydroxyl proton at 5.90 τ and broad absorption due to the phenyl protons between 2.68 and 2.96 τ.

(Pentachlorophenyl)trimethylsilane

A solution of trimethylchlorosilane (2.17 g, 0.02 mole, Matheson, Coleman and Bell) in 20 ml of tetrahydrofuran was added dropwise over a 20 min period to a stirring solution of pentachlorophenyllithium (0.02 mole) in 50 ml of tetrahydrofuran at −78°. After 40 min additional stirring at −78°, the solution was allowed to warm to room temperature with stirring over a 3.5 h period, filtered, and the solvent was removed. The residue was extracted with 30 ml of hot hexane, from which was obtained 3.1 g (48 % yield) of white crystals, m.p. 113–117°. An analytical sample was prepared by recrystallization from nitroethane following treatment with decolorizing charcoal; long white needles were obtained, m.p. 116.5–117.5°. (Found: C, 33.71; H, 2.92; Cl, 54.97; Si, 8.51. $C_9H_9Cl_5Si$ calcd.: C, 33.52; H, 2.79; Cl, 54.97; Si, 8.71 %.)

The IR spectrum (CS_2 soln.): 680, 850, 875, 1091, 1255, 1291, 2910, 2980 cm⁻¹. The NMR spectrum: singlet at 9.46 τ (CS_2 soln.); singlet at 9.46 τ (CCl_4 soln.).

Pentachlorobenzene

Distilled water (2.0 ml) was added dropwise from a syringe to a stirring solution of pentachlorophenyllithium (0.02 mole) in 50 ml of tetrahydrofuran at −78°. The mixture was then allowed to warm to room temperature with stirring over a 1 h period and was filtered. The filtrate was evaporated to produce a white residue, which on crystallization from ether gave 2.8 g (56 % yield) of white needles, m.p. 85–88°. On subsequent recrystallization from pentane, then from ethanol, a slightly purer product, m.p. 87.8–88.6° (reported[15] m.p. 85–86°), was obtained.

Characteristic IR absorption (CS_2 soln.): 680, 824, 863, 1088, 3070, 3110 cm⁻¹. The NMR spectrum exhibited a singlet in CS_2 soln. (2.58 τ) and in CCl_4 soln. (2.54 τ).

Pentachlorobenzoic acid

A 1-liter, 3-necked flask was fitted with a nitrogen inlet, mechanical stirrer and a condenser. The flask was flushed with nitrogen and a large amount of crushed dry ice was added and covered with anhyd. ethyl ether. The pentachlorophenyllithium solution (0.02 mole) in ethyl ether was carefully added to this slurry; a light yellow precipitate formed immediately. The mixture was stirred and allowed to warm to room temperature over a period of 24 h. The solid was dissolved by repeated washings with water. The extracts were acidified with 10 % sulfuric acid to produce 3.83 g (65 % yield) of a pale yellow solid, m.p. 205–207°. Subsequent recrystallization from benzene and from carbon tetrachloride raised the m.p. to 208.5–210° (reported[7] m.p. 207–211°).

The IR spectrum of this product was in excellent agreement with the spectrum reported for pentachlorobenzoic acid in the Satler Catalog of IR Spectra, No. 582.

A similar carbonation of pentachlorophenyllithium produced in tetrahydrofuran at −78° gave pentachlorobenzoic acid, m.p. 210–211.5°, in 56 % yield.

Bis(diethylphenylphosphine)pentachlorophenylnickel chloride

To a stirring solution of pentachlorophenyllithium (0.02 mole) in 50 ml of tetrahydrofuran at −78° was added over a 5 min period 4.56 g (0.01 mole) of bis(diethylphenylphosphine)nickel dichloride[3a,16]. After stirring for 4 h at −78°, the mixture was allowed to warm to room temperature over a two h period. The solvent was evaporated and the residue was sublimed at 150°/0.01 mm to remove hexachlorobenzene. The residue that remained was extracted with hot ethanol, and the extracts produced 4.05 g (60 % yield) of brown platelets, m.p. 132–133.5°. A slightly purer product, m.p. 132.5–134° (reported m.p. 133.5–135.5°)[3a] could be obtained by subsequent recrystallization from hexane.

Characteristic IR absorption (KBr pellet): 670, 835, 1108 cm⁻¹.

Bis(diethylphenylphosphine)bis(pentachlorophenyl)cobalt

Bis(diethylphenylphosphine)cobalt dichloride[3b]* (2.58 g, 0.0056 mole) was added over a 5 min period to a stirring solution of pentachlorophenyllithium (0.0225 mole) in 50 ml of tetrahydrofuran at −78°, and the reaction mixture was stirred at that temperature for an additional 4 h. The temperature was allowed to rise to 0°, the reaction mixture was hydrolyzed with 30 ml of water, and 2.1 g of a yellow-brown precipitate was obtained by filtration. Recrystallization from benzene produced lemon-yellow platelets, 1.63 g (33 % yield), m.p. 228–231° (reported[3b] m.p. 224–228°).

Characteristic IR absorption (KBr pellet): 669, 825, 1107 cm⁻¹.

Bis(pentachlorophenyl)mercury

A solution of mercuric chloride (2.72 g, 0.01 mole) in 120 ml of ethyl ether was added over a period of 1.5 h to pentachlorophenyllithium (0.02 mole) in 400 ml of the same solvent. The reaction temperature was maintained at −10° to 0°. A white precipitate formed immediately. The reaction mixture was allowed to warm to room temperature over a 2 h period, the solvent was evaporated and the residue was washed with hot water and dried (7.32 g). This material was digested three times with warm

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* The melting point of bis(diethylphenylphosphine)cobalt dichloride prepared in our Laboratory was 89–90° (reported[3b] m.p. 71–73°).

ethyl ether and once with hot water. After drying in air, white crystals remained, 5.83 g (84% yield), m.p. 380–382° (reported[9] m.p. 383°).

In a similar run using tetrahydrofuran as the solvent, a 66% yield of bis(pentachlorophenyl)mercury was obtained (m.p. 381–384°) following recrystallization from nitrobenzene.

Characteristic IR absorption (Nujol mull): 686, 856, 1091, 1176, 1202, 1300, 1330, 1518 cm^{-1}.

2,3,4,5,6-Pentachlorobenzhydrol

Five ml (0.0476 mole) of benzaldehyde was added to pentachlorophenyllithium (0.02 mole) in 400 ml of ethyl ether at —10° over a 10 min period. The reaction mixture was allowed to warm to room temperature for 2 h, was then hydrolyzed with 50 ml of water and the layers were separated. The ether layer was stirred for 20 min with 50 ml of satd. sodium bisulfite solution, and this process was repeated. The ether layer was washed with water and was dried over anhydr. sodium sulfate. The yellow solid (6.27 g) remaining after evaporation of the ether was crystallized from hexane to produce 5.74 g (81% yield) of light yellow crystals, m.p. 114–116° (reported[17] m.p. 117°).

Characteristic IR absorption (CCl$_4$ soln.): 688, 865, 1100, 1125 cm^{-1}.

Stability of pentachlorophenyllithium

(a) In ethyl ether. A solution of pentachlorophenyllithium (0.02 mole) in ethyl ether was prepared at —10° in the usual manner. At specified times and temperatures (Table 1), aliquots were withdrawn and added to a large excess of crushed dry ice. The reaction mixture was allowed to warm to room temperature, the ethyl ether was evaporated, the residue was extracted repeatedly with hot water and was filtered hot. After acidification of the hot filtrate with 10% sulfuric acid, the mixture was allowed to cool to room temperature, and the pentachlorobenzoic acid was filtered and dried. Melting point determinations indicated that essentially pure pentachlorobenzoic acid was formed in each case.

(b) In tetrahydrofuran. A solution of pentachlorophenyllithium (0.02 mole) in tetrahydrofuran was prepared at —78° in the usual manner. The analysis procedure was similar to that described in (a), except that hot 1 N potassium hydroxide solution was used to extract the lithium salt. The results are presented in Table 1.

SUMMARY

The action of n-butyllithium on hexachlorobenzene in ethereal solvents produces pentachlorophenyllithium in good yield. This new reagent has been characterized by the formation of a variety of pentachlorophenyl derivatives of Si, P, Hg, Ni, and Co, a well as organic derivatives. Pentachlorophenyllithium was found to exhibit moderate

stability in solution, especially in ethyl ether at —10° to 0°. The formation of penta
chlorophenyllithium in this manner represents the first example of a halogen–lithium
interconversion reaction involving a benzenoid aromatic chloride.

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