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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS
XIX*. SOME REACTIONS OF PENTACHLOROPYRIDINE WITH ORGANOMETALLIC COMPOUNDS

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SUMMARY

Some reactions of pentachloropyridine with organometallic compounds have been described. *n*-Butyl-, methyl-, phenyl- and triphenylsilyllithium are found to react, mainly by metathesis. The Grignard reagents, like benzylmagnesium chloride and ethylmagnesium bromide give coupling products with pentachloropyridine, at the 4-position. Phenylmagnesium bromide, methylmagnesium iodide and pentafluorophenyllithium did not react with pentachloropyridine. 4,4'-Octachlorobipyridine has been synthesized by three different methods. In the reaction of 4-(trimethylsilyl)tetrachloropyridine with n-butyllithium, the existence of the short-lived 2,3-pyridyne seems probable.

INTRODUCTION

In extension of studies on the chemistry of pentachloropyridine, a number of derivatives have been described; preliminary communications[1] include the reactions of pentachloropyridine with magnesium[1], n-butyllithium[2] and various nucleophiles. In continuation of our earlier studies on the derivatives of pentachloropyridine, we describe here some reactions of pentachloropyridine with organometallic compounds in tetrahydrofuran (THF) or THF/ether mixture.

RESULTS AND DISCUSSION

Addition of methyl- or n-butyllithium to an equimolar amount of pentachloropyridine in THF at −70° resulted in a rapid metathetical reaction. From the red-colored solution, after stirring for six hours followed by the addition of chlorotrimethylsilane, heptachlorobipyridine (of unknown orientation) was isolated. The NMR spectrum of this compound showed a singlet at 2.9 τ (lit.[2] singlet, 2.83 τ). The formation of heptachlorobipyridine could be explained in terms of the decomposition of tetrachloropyridyllithium (I), followed by the reaction of the short-lived intermediate with (I):

$$C_5Cl_5N \xrightarrow{\text{BuLi}} C_5Cl_4N(Li) \rightarrow [C_5Cl_3N] \xrightarrow{\text{(I)}} \text{heptachlorobipyridine}$$

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* For Part XVIII see ref. 6.

The existence of such reactive intermediates has earlier been established in the interesting studies by Cook and Wakefield[2]. However, an immediate reaction of (I) with chlorotrimethylsilane gave the expected 4-(trimethylsilyl) tetrachloropyridine in satisfactory yield[1].

A similar reaction of pentachloropyridine in THF with phenyllithium gave 4,4'-octachlorobipyridine (50% yield) but no heptachlorobipyridine has been isolated. In this case, a rapid exchange followed by the coupling of $C_5Cl_4N(Li)$ with the remaining pentachloropyridine, is the probable course of the reaction. Attempts to isolate biphenyl were not successful; however, chlorobenzene was a reaction product. The structure of 4,4'-octachlorobipyridine was confirmed by an independent synthesis of this compounds from 4-tetrachloropyridylmagnesium chloride and pentachloropyridine.

From the reaction of triphenylsilyllithium[3] with pentachloropyridine in THF at $-70°$, hexaphenyldisilane (II), 4,4'-octachlorobipyridine (III) and 4-(triphenylsilyl)-tetrachloropyridine (IV) could be obtained. The compounds (II) and (III) were characterized by mixing melting points with authentic samples. The identity of (IV) was established by the synthesis of this compound from 4-tetrachloropyridylmagnesium chloride and chlorotriphenylsilane.

$$Ph_3SiLi + C_5Cl_5N \rightarrow Ph_3SiCl + C_5Cl_4N(Li)$$

$$Ph_3SiCl + Ph_3SiLi \rightarrow Ph_3SiSiPh_3 + LiCl$$

$$C_5Cl_4N(Li) + C_5Cl_5N \rightarrow C_{10}Cl_8N_2$$

$$C_5Cl_5N + Ph_3SiLi \rightarrow 4\text{-}Ph_3SiC_5Cl_4N$$

It was earlier shown[4] that hexachlorobenzene undergoes a halogen–metal exchange to a small extent. In an attempt to prepare 4-tetrachloropyridylmagnesium chloride, by an exchange reaction between pentachloropyridine and benzylmagnesium chloride, it was found that the main reaction was coupling to give 4-benzyltetrachloropyridine (V), in satisfactory yield. The NMR spectrum of this compound showed singlets at 5.7 τ (CH_2 protons) and 2.85 τ (aromatic protons). To lend supporting evidence to the coupling position, (V) was oxidised, employing sodium dichromate and sulfuric acid. No known acid could be isolated. The product from this reaction was identified as benzoyltetrachloropyridine, on the basis of IR, NMR and mass spectra. By analogy with 4-ethyltetrachloropyridine (see below), it appears reasonable that the coupling occurred at the 4-position in the pentachloropyridine and benzylmagnesium chloride reaction, if one can assume no rearrangement.

A similar reaction of pentachloropyridine with ethylmagnesium bromide gave a crystalline solid (45% yield) identified as 4-ethyltetrachloropyridine, by comparison with the sample obtained from 4-tetrachloropyridylmagnesium chloride and ethyl iodide. The NMR spectrum of this compound showed resonances characteristic of an ethyl group (quartet, 6.92 τ and triplet, 8.72 τ).

All attempts to prepare phenyl, methyl and pentafluorophenyl tetrachloropyridines by the reaction of the corresponding Grignard reagents with pentachloropyridine have so far been unsuccessful. At this stage, it seems, steric factors may be significant.

With a view to preparing bis- and tris(trimethylsilyl)polychloropyridines from 4-(trimethylsilyl)tetrachloropyridine, n-butyllithium and chlorotrimethylsilane, in THF, a liquid was isolated. The NMR spectrum of this liquid showed resonances characteristic of n-butyl, trimethylsilyl and aromatic protons. The intermediate formation of the hitherto unknown 2,3-pyridyne seems probable. The investigation is in progress and details will appear later.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Tetrahydrofuran was dried over sodium followed by distillation from sodium benzophenone ketyl. n-Butyl-, methyl- and phenyllithium were from the Foote Mineral Corporation. IR, NMR and UV spectra were determined employing PE-21 infrared, A-60 NMR and Cary 14R spectrometers, respectively. All melting points are uncorrected.

Pentachloropyridine and methyllithium

Pentachloropyridine (5 g, 0.02 mole) in 50 ml of THF was added dropwise, with stirring, to methyllithium (0.02 mole) in ether at −70°. The resulting solution was red in color. After stirring for six h, chlorotrimethylsilane (5 g, 0.04 mole) was added and stirring was continued for an additional two h. The solvent was removed under reduced pressure and the residue, after hydrolysis, was taken up in ether. The ether extract was dried ($MgSO_4$) and the solvent was stripped off under reduced pressure to give 2.2 g (55 %) of a solid, m.p. 176–178°, after crystallization from methanol, identified as heptachlorobipyridine. of unknown orientation. The NMR spectrum of this compound showed a singlet at 2.9 τ (lit.[2] singlet, 2.83 τ).

Pentachloropyridine and phenyllithium

A similar reaction, employing pentachloropyridine (5 g, 0.02 mole) in THF and phenyllithium (10 ml, 0.02 mole) at −70°, gave after hydrolysis and work-up 2.1 g (49 %) of a solid, m.p. 226–228°, after crystallization from petroleum ether (b.p. 60–70°). This compound was identified as 4,4′-octachloropyridine, by a mixed m.p. with the sample obtained, in 32 % yield, from 4-tetrachloropyridylmagnesium chloride and pentachloropyridine in THF (Found: C, 28.04; mol. wt., 432. $C_{10}Cl_8N_2$ calcd.: C, 27.78 %; mol. wt., 432.)

Pentachloropyridine and triphenylsilyllithium

Triphenylsilyllithium (0.02 mole), prepared from hexaphenyldisilane and lithium in THF, employing a reported procedure[3], was added to pentachloropyridine (5 g, 0.02 mole) in THF at −70°. The resulting solution assumed a red color. After stirring for six h, chlorotrimethylsilane (5 g, 0.04 mole) was added and stirred for an additional three h. The solvent was removed and the residue extracted with benzene. The benzene-insoluble portion gave 4.5 g (85 %) of a solid, characterised as hexaphenyldisilane, m.p. 362–364°, after crystallisation from benzene. A mixed m.p. with an authentic sample was undepressed.

From the benzene-soluble portion, after removal of benzene and fractional crystallisation from petroleum ether (b.p. 60–70°), were isolated two solids (VI), m.p. 226–228°, (VII), m.p. 247–249° (both in less than 6% yield). Compound (VI) was identified as 4,4'-octachlorobipyridine (mixed m.p. with the sample obtained from 4-tetrachloropyridylmagnesium chloride and pentachloropyridine).

Compound (VII) was found identical, in all respects, with that obtained, in 50% yield, from 4-tetrachloropyridylmagnesium chloride and chlorotriphenylsilane in THF. It is, therefore, 4-(triphenylsilyl)tetrachloropyridine (Found: C, 58.17; H, 3.36; mol.wt., 475. $C_{23}H_{15}Cl_4NSi$ calcd.: C, 58.10; H, 3.16%; mol.wt., 475.)

Pentachloropyridine and ethylmagnesium bromide

Ethylmagnesium bromide (0.02 mole) in ether was added dropwise with stirring, to pentachloropyridine (5 g, 0.02 mole) in THF, at room temperature and stirred over night. The customary work-up gave 2.2 g (45%) of a solid, m.p. 74–75°, after crystallisation from methanol. The NMR spectrum of this compound showed a quartet (6.92 τ) and a triplet (8.72 τ), characteristic of an ethyl group. The identity of this compound as 4-ethyltetrachloropyridine was established by an independent synthesis, in 54% yield, from 4-tetrachloropyridylmagnesium chloride and ethyl iodide in THF; mixed m.p. was undepressed (Found: C, 34.37; H, 2.09; mol.wt., 245. $C_7H_5Cl_4N$ calcd.; C, 34.28; H, 2.04%; mol.wt., 245.)

Pentachloropyridine and benzylmagnesium chloride

Benzylmagnesium chloride (0.05 mole) in ether was added to pentachloropyridine (12.5 g, 0.05 mole) in THF at 0°. The reaction was highly exothermic and there was immediate formation of a thick white precipitate. Thirty min after the addition of benzylmagnesium chloride, Color Test I[5] of the reaction mixture was negative. The work-up gave 11.5 g (74%) of a solid, m.p. 107–108°, after crystallisation from 95% ethanol. The identity of this compound as 4-benzyltetrachloropyridine was established on the basis of its NMR spectrum, singlets at 5.7 τ (CH_2 protons) and 2.85 τ (aromatic protons). The UV spectrum (CCl_4) showed two absorption maxima: λ_{max} (log ε): 292 mμ (3.62), 255 mμ (3.32). (Found: C, 47.05; H, 2.25; mol.wt., 307. $C_{12}H_7Cl_4N$ calcd.: C, 46.91; H, 2.28%; mol.wt., 307.)

Oxidation of 4-benzyltetrachloropyridine

4-Benzyltetrachloropyridine (2 g, 0.0065 mole) was mixed with sodium dichromate (15 g), concentrated sulfuric acid (15 ml), glacial acetic acid (50 ml) and water (15 ml) and refluxed for four h. The mixture was poured in ice-cold water and extracted with 3 × 50 ml of chloroform. The chloroform extract was dried ($MgSO_4$) and the solvent was removed to give 1.2 g (57%) of 4-benzoyltetrachloropyridine, m.p. 134–135°, after crystallisation from ethanol. The IR spectrum of this compound showed a very strong absorption at 5.92 μ, indicating a carbonyl group. The NMR spectrum (CCl_4) showed a singlet at 2.7 τ, characteristic of aromatic protons. The UV spectrum of this compound (CCl_4) contained a band at 292 mμ with log ε 3.82. (Found: C, 44.65; H, 1.83; mol.wt., 321. $C_{12}H_5Cl_4NO$ calcd.: C, 44.86; H, 1.56%; mol.wt., 321.)

Similar reactions of pentachloropyridine with phenylmagnesium bromide, methylmagnesium iodide and pentafluorophenyllithium have so far been unsuccessful. No coupling products have been isolated. The recovery of pentachloropyridine, in these reactions, was of the order of 80–85%.

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