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SHORT COMMUNICATION

Polyhalo-organometallic and -organometalloidal compounds IX*. The reaction of n-butyllithium with (pentafluorophenyl)trimethylsilane

As part of a study on the general comparison of polyfluoro and polychloro compounds and on the preparation of tetrakis(trimethylsilyl)allene from polyfluorophenyl compounds[1], it was necessary to prepare 1,4-bis(trimethylsilyl)tetrafluorobenzene (I). This compound was simply prepared in 81 % yield by the reaction between 1,4-dilithiotetrafluorobenzene[2] and chlorotrimethylsilane. However, it had previously been shown in these laboratories[3] that 1,4-bis(trimethylsilyl)tetrachlorobenzene could be prepared by the reaction of n-butyllithium (x moles) with (pentachlorophenyl)trimethylsilane (x moles) in THF at −65° followed by treatment with chlorotrimethylsilane. It was of interest, therefore, to compare a similar series of reactions with (pentafluorophenyl)trimethylsilane as a possible route to (I).

Addition of n-butyllithium in hexane to a solution of (pentafluorophenyl)-trimethylsilane in THF at −65° resulted in the consumption of all the organometallic species during 1 hour. Work-up gave a product (II) the NMR spectrum of which contained an absorption at τ 9.6 ppm characteristic of a trimethylsilyl group and absorptions at 7.3, 8.5 and 9.05 ppm characteristic of an n-butyl group. The integrated area ratio of the trimethylsilyl to butyl protons was 1 : 1. This evidence, together with the molecular weight and elemental analysis, indicated that the compound contained a tetrafluorobenzene ring substituted by an n-butyl group and a trimethylsilyl group.

Treatment of (II) with 10% sodium hydroxide in THF at room temperature gave (III), which appeared from its elemental analysis and molecular weight to be a butyl-substituted tetrafluorobenzene. The ^{1}H NMR spectrum of (III) showed absorptions at τ 7.3, 8.5 and 9.05 ppm characteristic of the n-butyl group and an absorption centered around 3.15 ppm characteristic of an aromatic proton. The integrated area ratio of the aromatic to butyl protons was 1 : 9. The aromatic proton absorption at 3.15 ppm was split into a symmetrical 9 line pattern of the type expected for an aromatic proton coupled with two *o*- and two *m*-fluorine atoms. The observed coupling constants [J(*o*-F–H) 10 cps, J(*m*-F–H) 6 cps] were similar to those reported for this type of system[4]. This evidence suggested that (III) was n-butyl-2,3,5,6-tetrafluorobenzene and that (II) was therefore 1-(trimethylsilyl)-4-n-butyltetrafluorobenzene.

Experiments were then carried out to confirm rigorously the positions of the substituents. Treatment of 2,3,5,6-tetrafluorophenyllithium in ether or THF with an excess of n-butyl bromide gave no detectable quantity of (III). However, this was not surprising as it has been reported[5] that treatment of 2,3,5,6-tetrafluorobromobenzene with n-butyllithium in ether gave 2,3,5,6-tetrafluorophenyllithium and, presumably, n-butyl bromide.

It has been shown that certain trialkyl phosphates frequently have advantages

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* For Part VIII see ref. 11.

over the alkyl halides in the alkylation of organometallic compounds[6]. For this reason the reaction of 2,3,5,6-tetrafluorophenyllithium with tri-n-butyl phosphate at −65° was investigated as a possible route to (III). In ether, no alkylation appeared to occur as no (III) could be detected by VPC even after the reaction mixture was allowed to warm to room temperature. However, when THF was used as solvent a 24% yield of (III) was obtained.

Compound (III) was converted to (II) in 70% yield by treatment with n-butyllithium in THF at −65° followed by treatment with chlorotrimethylsilane.

The nucleophilic attack of an alkyllithium compound on a perfluorophenyl compound is not unusual. For instance, it has been shown that hexafluorobenzene reacts with methyllithium in THF[7] or ether[8] at low temperatures to give 65–75% yields of pentafluorotoluene; a similar reaction[7] with n-butyllithium in THF gave 56% of n-butylpentafluorobenzene. It is therefore not surprising that (II) was obtained in 54% yield from the reaction of n-butyllithium with (pentafluorophenyl)trimethylsilane. However, the marked difference between (pentafluorophenyl)trimethylsilane and (pentachlorophenyl)trimethylsilane is of interest.

Experimental

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Ethereal solvents were dried over sodium followed, in the case of THF, by distillation from sodium benzophenone ketyl. n-Butyllithium in hexane was obtained from Foote Mineral Corporation. Molecular weights were determined by mass spectrometry. NMR spectra were recorded in CCl_4 with a Varian A60 spectrometer.

1,4-Bis(trimethylsilyl)tetrafluorobenzene. 1,2,4,5-Tetrafluorobenzene (15 g, 0.1 mole) in THF (20 ml) was added to n-butyllithium (0.2 mole) in THF (270 ml) at −65°. After 60 min Color Test II[9] was negative indicating that all the n-butyllithium had been consumed. Chlorotrimethylsilane (21.7 g, 0.2 mole) in THF (50 ml) was added during 15 min, and Color Test I[10] was negative immediately after the addition. The reaction mixture was allowed to warm to room temperature, concentrated, the residue extracted with petroleum ether (b.p. 60–80°), filtered and the residue concentrated leaving a white solid which on crystallization from methanol gave 1,4-bis(trimethylsilyl)tetrafluorobenzene, 24.8 g, 81.0%. (Found: C, 49.3; H, 6.23; mol. wt., 294. $C_{12}H_{18}F_4Si_2$ calcd.: C, 49.0; H, 6.13%; mol. wt., 294.3.)

Reaction of n-butyllithium with (pentafluorophenyl)trimethylsilane. n-Butyllithium (0.05 mole) in hexane was added to a solution of (pentafluorophenyl)trimethylsilane (12.0 g, 0.05 mole) in THF (75 ml) at −65°. The solution turned slightly red and after 30 min Color Test I was negative. The reaction mixture was worked up as described above to give a liquid product which was distilled under reduced pressure to give 1-(trimethylsilyl)-4-butyltetrafluorobenzene, b.p. 77°/0.6 mm, n_D^{20} 1.4595, 7.5 g, 54%. (Found: C, 55.96; H, 6.74; mol. wt., 278. $C_{13}H_{18}F_4Si_2$ calcd.: C, 56.1; H, 6.49%; mol. wt., 278.2.)

Five g of the above material was dissolved in THF (25 ml) and 10% sodium hydroxide (5 ml) was added. The solution was stirred for 2 h when VPC showed that no starting material remained. The ethereal layer was separated, dried, concentrated and the residue distilled to give n-butyl-2,3,5,6-tetrafluorobenzene, b.p. 64°/12 mm, n_D^{20} 1.4350, 2.9 g, 78.5%. (Found: C, 58.6; H, 5.1; mol. wt., 206. $C_{10}H_{10}F_4$ calcd.: C, 58.3; H, 4.9%; mol. wt., 206.1.)

Reaction of 2,3,5,6-*tetrafluorophenyllithium with tri-n-butyl phosphate.* 1,2,4,5-Tetrafluorobenzene (15 g, 0.1 mole) in THF (200 ml) was cooled to −65°. n-Butyllithium (0.1 mole) in hexane was added dropwise with stirring during 1 h. Color Test II was negative after the addition. A solution of tri-n-butyl phosphate (23.6 g, 0.1 mole) was added during 30 min. The reaction mixture was stirred 12 h at −65° when Color Test I was still positive. The reaction mixture was allowed to warm to room temperature during 5 h, in which time it turned black, and Color Test I became negative. Following acid hydrolysis, the ethereal layer was dried, concentrated and the residue distilled to give 5.0 g, 24% of n-butyl-2,3,5,6-tetrafluorobenzene, b.p. 64–65°/12 mm. n_D^{20} 1.4349.

Preparation of 1-*trimethylsilyl-4-n-butyltetrafluorobenzene from n-butyl*-2,3,5,6-*tetrafluorobenzene.* n-Butyl-2,3,5,6-tetrafluorobenzene (4 g, 0.02 mole) was dissolved in THF (50 ml) at −65° and n-butyllithium (0.02 mole) was added during 5 min. Color Test II was negative immediately after the addition. Chlorotrimethylsilane (6 g, excess) was added and the mixture was allowed to warm to room temperature, before being concentrated and the residue treated with pentane and filtered. Concentration of the pentane solution and distillation of the residue under reduced pressure gave 3.9 g, 70% of 1-(trimethylsilyl)-4-n-butyltetrafluorobenzene, b.p. 70–71°/0.2 mm, n_D^{20} 1.4593.

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