Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

(PENTAFLUOROPHENYL)MAGNESIUM CHLORIDE

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(Received January 21st, 1969)

In connection with studies concerning the preparation and reactions of polyhaloorganometallic compounds[1] we have prepared (pentafluorophenyl)magnesium chloride (C_6F_5MgCl) in THF**. The recent report of the preparation of pentafluorophenyllithium from chloropentafluorobenzene and n-butyllithium[2] prompted us to report details for the preparation of C_6F_5MgCl in tetrahydrofuran rather than in ether[3]. Our method is convenient, affords the Grignard reagent in high yield, and may be economically advantageous as chloropentafluorobenzene is a product in the preparation of hexafluorobenzene from hexachlorobenzene. Furthermore, pentafluorophenyl–metallic compounds can be prepared without the use of another organometallic compound.

Pentafluorophenyl–Grignard reagents have been prepared by several methods: (1) directly from chloro-[3], bromo-[4], and iodopentafluorobenzene[5] and magnesium in ether, and also from bromopentafluorobenzene in THF[6] at a low temperature; (2) by an exchange reaction between pentafluorobenzene and excess ethylmagnesium bromide[7]; and (3) by a rapid exchange between bromopentafluorobenzene and ethylmagnesium bromide[8]. (Pentafluorophenyl)magnesium bromide was found to be stable in THF solution at the ambient temperature over a period of 5 days, although 70% decomposition occurred on refluxing a THF solution for 24 h[8] (*cf.* the great stability of these Grignard reagents in refluxing ether*).

Previously, the reported attempted preparation of C_6F_5MgCl from chloropentafluorobenzene and magnesium in refluxing THF[3] had given polymeric material as the sole product. We have found that this Grignard reagent is formed in high yield from chloropentafluorobenzene and magnesium in THF at −10°. Addition of an initiator such as iodine or 1,2-dibromoethane was not required. On monitoring the preparation by GLC it was found that at 20, 30, 45 and 60 min after commencement 80, 90, 95 and 99%, respectively, of the chloropentafluorobenzene had been consumed. The yield of the Grignard reagent by titration in three separate preparations was 92, 95, and 99% although the method employed is reported to give figures that may be a few percent high[9].

A THF solution of C_6F_5MgCl kept at the ambient temperature (*ca.* 28°) had

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* For a review of polyhaloorgano-Grignard reagents and lithium compounds see ref. 18; for a review of pentafluorophenyl–metallic compounds see ref. 19.

** We have just learned of a recent preparation of C_6F_5MgCl in THF[20].

partly decomposed in 16.5 h, as shown by the formation of an insoluble white solid[10]. To this mixture was added an excess of chlorotrimethylsilane. The products were trimethyl(pentafluorophenyl)silane (46.5%) and a white solid (m.p. >360°) which appeared to be similar to that isolated from the decomposition of C_6F_5MgBr in THF[10]. When chlorotrimethylsilane was added immediately after the Grignard reagent had been prepared, trimethyl(pentafluorophenyl)silane was isolated in 78% yield. No explanation is advanced for the difference in stability of THF solutions of C_6F_5MgBr and C_6F_5MgCl. It is recommended that the Grignard reagent prepared by this method be used within a few hours, preferably at about 0°.

Addition of mercuric chloride to the Grignard reagent gave (pentafluorophenyl)mercuric chloride and bis(pentafluorophenyl)mercury in 73% and 84% yields, respectively. Other workers in this laboratory have used the Grignard reagent prepared by this method to obtain triphenyl(pentafluorophenyl)lead from triphenyllead chloride in 54% yield[11].

Addition of copper(I) iodide to the Grignard reagent in THF at 0° gave a (pentafluorophenyl)copper compound or complex[1,12,13] and subsequent reaction of this with acetyl chloride gave a 69.5% yield of 2′,3′,4′,5′,6′-pentafluoroacetophenone. Previously we have reported the isolation of decachlorotolan in 8% yield from addition of cobalt chloride and tetrabromoethylene to (pentachlorophenyl)magnesium chloride[1]. In a similar reaction with C_6F_5MgCl, first at 0° and then while slowly allowing the temperature of the mixture to rise and eventually in refluxing THF, no decafluorotolan was isolated. The relative instability of C_6F_5MgCl may be one of the significant factors in the failure of the latter reaction.

EXPERIMENTAL

The reactions were carried out in an atmosphere of nitrogen. Tetrahydrofuran was dried over sodium and distilled prior to use from sodium–benzophenone ketyl. Magnesium metal turnings were from the Mallinckrodt Chemical Works and chloropentafluorobenzene was purchased from the Whittaker Corporation. All temperatures quoted are uncorrected.

(Pentafluorophenyl)magnesium chloride

Chloropentafluorobenzene (20.26 g, 0.10 mole) in THF (150 ml) was stirred with magnesium turnings (2.75 g, 0.11 g-atom) at the ambient temperature until a pale yellow color developed, and then cooled to −10° (ice-salt bath). Stirring was continued and the mixture examined periodically by GLC on a 36 × $\frac{1}{4}$″ column of DC silicone oil 710 on chromosorb. By comparison with standard solutions of chloropentafluorobenzene in THF it was determined that at 20, 30, 45 and 60 min after commencement, 80, 90, 95 and 99%, respectively, of the chloropentafluorobenzene had been consumed. The mixture was stirred for a further 20 min to ensure complete reaction and then filtered. The THF solution of the Grignard reagent was brown to purple in color and gave Color Test I[14], although the malachite green color was slow (4 min) in development. Titration of an aliquot (2 ml) by addition to excess hydrochloric acid and back titration with sodium carbonate solution indicated that the Grignard reagent had been prepared in 92% yield. After addition of powdered mercuric chloride (30.0 g) the mixture was stirred for 15 h at 0°. The customary work-up gave (pentafluorophenyl)mercuric chloride (29.42 g, 73%), m.p. 164–165°. Crystallization from a carbon tetrachloride/light petroleum (b.p. 60–70°) mixture afforded a sample m.p. 164.5–165.5° [cited[15]: 165°].

In a similar preparation of C_6F_5MgCl (from 0.10 mole C_6F_5Cl), titration indicated a yield of 95%. Subsequent to addition of mercuric chloride (12.22 g, 0.045 mole) there was obtained pale yellow needles (22.60 g), m.p. 138–140°. Sublimation and crystallization from CCl_4 afforded white needles of bis(pentafluorophenyl)mercury[15,16] (20.30 g, 84%), m.p. 140.5–141.5[cited[15]: 142.3°].

Reaction with chlorotrimethylsilane

The Grignard reagent was prepared as before (from 0.10 mole C_6F_5Cl): by titration the yield was 99%. An excess of chlorotrimethylsilane (15 ml) was added to the Grignard reagent at 0° and the mixture stirred for several hours. Subsequent to the usual work-up and distillation there was obtained trimethyl(pentafluorophenyl)silane (18.77 g, 78 %), b.p. 64.5°/14 mm, 172–173° [cited[17]: 60°/14 mm, 170°] with an IR spectrum identical to that reported.

In a similar reaction but with filtration of the Grignard reagent after 40 min, the yield of trimethyl(pentafluorophenyl)silane was 71.5%.

Stability of (pentafluorophenyl)magnesium chloride

The Grignard reagent (prepared from 0.10 mole C_6F_5Cl) in THF was kept at the ambient temperature (*ca.* 28°) for 16.5 h. As an insoluble, white solid formed during this time, an excess of chlorotrimethylsilane (15 ml) was added, after cooling to 0°. The customary work-up afforded trimethyl(pentafluorophenyl)silane (11.15 g, 46.5%), b.p. 172–173°, and an insoluble, white solid (6.75 g), m.p. > 360°. This material appears to be of the same type as that isolated from the decomposition of pentafluorophenyl–Grignard reagents in THF[10].

Reaction with copper(I) iodide, followed by acetyl chloride

To the Grignard reagent (prepared from 0.10 mole C_6F_5Cl) at 0° was added copper(I) iodide (20.5 g) and the mixture stirred at 0° for 36 h. Subsequent to addition of acetyl chloride (10 ml) there was obtained 2′,3′,4′,5′,6′-pentafluoroacetophenone (14.63 g, 69.5%), b.p. 97–98°/50 mm, with an IR spectrum in agreement with that reported[5].

ACKNOWLEDGEMENTS

This research was supported by the United States Air Force under Contract F33615–68–C–1251 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright–Patterson AFB, Ohio.

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