Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

Preliminary Note

The reaction of bromotetrafluorophenyl mercurials with magnesium

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(Received November 1st, 1971)

Although many bromotetrafluorophenyl derivatives of metals and metalloids undergo Li/Br exchange with n-butyl-lithium in ether/hexane[1], the corresponding reactions involving bromotetrafluorophenyl mercurials occur with a preferential Li/Hg exchange[1,2].

In order to investigate reactions at the C–Br bond, formation of the Grignard reagent was attempted by the substitution of magnesium for n-butyl-lithium. Bis-(3-bromotetrafluorophenyl)mercury and magnesium (in a 1:2 reactant ratio) did not react after heating in refluxing ether overnight. Substitution of tetrahydrofuran, however, followed by hydrolysis, ether extraction and solvent removal, gave a 20% yield of bis-(3-hydrotetrafluorophenyl)mercury, identified by a comparison of its infrared and ^{1}H NMR spectra with an authentic sample, prepared in 64% yield by the reaction of 1-lithio-3-hydrotetrafluorobenzene with mercuric chloride in ether/hexane[3].

Filtration of the hydrolyzed reaction mixture gave mercury and mercuric iodide (probably from reaction between mercury and the iodine added to initiate the Grignard formation) in yields that would account for 80% loss of the organo mercurial. This observation suggests the possible formation of tetrafluorophenylmagnesium derivatives and subsequent hydrolysis to tetrafluorobenzenes, which would be removed during solvent evaporation.

The above reaction was repeated using magnesium and the mercurial in 3:1 ratio and after ether extraction, analyzed by vapor phase chromatography. 1-Hydro-3-bromotetrafluorobenzene was the only polyfluoroarene detected and provides good evidence for the formation of bis-(3-bromotetrafluorophenyl)-magnesium. This provides an additional method for the synthesis of bis-(polyfluoroaryl)magnesium derivatives[4, 5], and is shown to be of general use by the reaction between magnesium and bis-(pentafluorophenyl)mercury in refluxing tetrahydrofuran for 12 h, when addition of trimethylchlorosilane gave the expected pentafluorophenyltrimethylsilane in quantitative yield.

The above procedure was repeated for bis-(4-bromotetrafluorophenyl)-mercury. Use of the mercurial and magnesium in a 1:2 ratio gave bis-(4-hydrotetrafluorophenyl)mercury in 5% yield, identified by ^{1}H NMR and mass spectroscopy. When an excess of magnesium (> 3:1 ratio) was employed, tetrafluorobenzenes were not detected by VPC analysis of the resultant ether solution. Removal of ether did, however, produce a mixture of bis-(4-hydrotetrafluorophenyl)mercury and a polyfluoropolyphenyl, identified by a comparison of its infrared spectrum with previous observations [5].

For comparison purposes, the corresponding reactions of the unfluorinated mercurials were investigated. No reaction was observed between bis-(3-bromophenyl)mercury and magnesium in refluxing tetrahydrofuran over several days. With the 4-bromophenyl mercurial, however, benzene and bromobenzene were detected by VPC analysis. Removal of solvent gave a solid, indicated by its infrared spectrum to be a mixture of diphenylmercury and unreacted bis-(4-bromophenyl)-mercury, the latter being 75% recovered. For this reaction, therefore, all possible magnesium derivatives, *i.e.*, $(4\text{-BrMgC}_6\text{H}_4)_2\text{Hg}$, $(4\text{-BrMgC}_6\text{H}_4)_2\text{Mg}$ and $(4\text{-BrC}_6\text{H}_4)_2\text{Mg}$, are being formed, but the Hg/Mg exchange reaction appears to be of less importance than for the polyfluoroaryl mercurials.

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