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Cleavage of pentafluorophenyl–phosphorus and –sulfur bonds by ethylmagnesium bromide

Stephen A. Sicree and Christ Tamborski*
Christ Tamborski - Fluidics Inc., P.O. Box 291886, Dayton, OH, 45429 (USA)

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Abstract

Tris(pentafluorophenyl) phosphine and bis (pentafluorophenyl) sulfide react with ethylmagnesium bromide to give products indicating cleavage of the pentafluorophenyl group from phosphorus and sulfur. Ethylated phosphorus and sulfur compounds as well as pentafluorophenylmagnesium bromide are the principal reaction products. Minor products from subsequent reaction between the Grignard reagents and cleavage products have also been detected.

Introduction

Alkyl Grignard reagents react with perfluoroaromatic compounds by nucleophilic substitution of aromatic fluorine to yield alkylated perfluoroaromatic compounds [1]. In our present study, we have attempted to ethylate substituted perfluoroaromatics, e.g. $(C_6F_5)_3P$ and $(C_6F_5)_2S$, using ethylmagnesium bromide in the expectation that an ethylated fluoroaromatic phosphine and sulfide would be formed. The results however indicated that the predominant reaction is not one of nucleophilic substitution of the fluoroaromatic ring, but instead cleavage of the phosphorus–pentafluorophenyl and sulfur–pentafluorophenyl bonds to yield ethylated phosphorus and sulfur derivatives as the principal products.

$$(C_6F_5)_3P + C_2H_5MgBr \longrightarrow (C_6F_5)_2PC_2H_5 + C_6F_5MgBr \tag{1}$$

$$(C_6F_5)_2S + C_2H_5MgBr \longrightarrow C_6F_5SC_2H_5 + C_6F_5MgBr \tag{2}$$

Pentafluorophenyl [2–4] and trifluorovinyl [5] groups bonded to a metal, e.g. Sn, and a metalloid, e.g. Si, are known to be cleaved by organomagnesium and organolithium compounds to yield perfluoroaryl– or perfluorovinyl–magnesium and -lithium compounds.

In these examples, the Sn and Si are rendered more electrophilic by the inductive effect of the C_6F_5 or $CF_2{=}CF$ groups, which aid a nucleophilic attack of the $C_6H_5^-$ or $C_2H_5^-$ ion from the organometallic reagent on the metal or metalloid. The resulting cleavage of the R_f group from the Sn or Si yields a new perfluoroorganometallic compound. Similar bond ruptures

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have been effected by a fluoride ion, resulting in the cleavage of the R_f group from a metal, e.g. Hg [6, 7] or Si [8–10]:

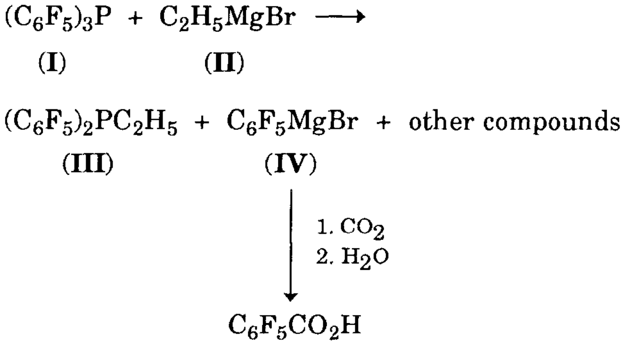
$$R_fM{\equiv} + F^- \longrightarrow R_f^- + {\equiv}MF \qquad (3)$$

Generation of such perfluoroanions have synthetic value as reported by the reactions of the R_f^- ion (where $R_f = CF_3$) with numerous ketones to yield CF_3-substituted alcohols in excellent yield [10].

It was, however, surprising to observe that compounds containing the non-metallic elements sulfur and phosphorus attached to a pentafluorophenyl group are also capable of cleavage by an organometallic such as C_2H_5MgBr. Whether other elements containing an R_f group behave similarly is yet to be determined. In some related work, the polyfluoronorbane–sulfur bond in the compound bis(undecafluorobicyclo[2,2,1]heptan-1-yl)disulfide was ruptured by either zinc in acetic acid or sodium borohydride in diglyme [11]

Results and discussion

Within a few minutes after the addition of C_2H_5MgBr to $(C_6F_5)_3P$ in tetrahydrofuran, an exothermic reaction occurred. After carbonation of the reaction mixture and work-up of the products, two principal compounds were isolated, $(C_6F_5)_2PC_2H_5$ and $C_6F_5CO_2H$. GC–MS analysis of the reaction mixture also indicated a number of minor products whose identity was partially resolved from the mass spectral data.



$$\underset{\textbf{(I)}}{(C_6F_5)_3P} + \underset{\textbf{(II)}}{C_2H_5MgBr} \longrightarrow \underset{\textbf{(III)}}{(C_6F_5)_2PC_2H_5} + \underset{\textbf{(IV)}}{C_6F_5MgBr} + \text{other compounds} \qquad (4)$$

$$C_6F_5MgBr \xrightarrow{1.\ CO_2;\ 2.\ H_2O} C_6F_5CO_2H$$

From the mass spectral data of the minor components, it appears that they may result from further reaction of the two Grignard reagents **II** and **IV** with either **I** or **III**. In any event, the substitution of the aromatic fluorines by C_2H_5MgBr and C_6F_5MgBr is minimal. This is in sharp contrast to the reaction between C_6F_5Li and $(C_6F_5)_3P$, where substitution of the aromatic fluorine takes place exclusively [12].

Under identical conditions to those described for the $(C_6F_5)_3P$ cleavage, the reaction between C_2H_5MgBr and $(C_6F_5)_2S$ also resulted in some cleavage. Only about 12% of $(C_6F_5)_2S$ was cleaved, indicating a slower rate of reaction. If, however, the reaction was allowed to proceed for a longer period (7 h), 85% of $(C_6F_5)_2S$ reacted producing $C_6F_5SC_2H_5$ as the major product. No $C_6F_5CO_2H$ (from the carbonation of C_6F_5MgBr) was found.

$$\underset{(VI)}{C_6F_5SC_6F_5} + \underset{(II)}{C_2H_5MgBr} \longrightarrow \underset{(VII)}{C_6F_5SC_2H_5} + \underset{(IV)}{C_6F_5MgBr} \qquad (5)$$

Since no $C_6F_5CO_2H$ was isolated (after carbonation), **IV** as well as **II** further reacted with **VI** and **VII** to give other ethylated and perfluorophenylated products. (See Experimental section – products C, D, E and F.)

From these observations it appears that, due to the inductive effect of the C_6F_5 group, the $C_6F_5^-P^+$ bond is more polarized than the $C_6F_5^-S^+$ bond, and thus reacts at a faster rate with the base $C_2H_5^-$. Other metals and metalloids, e.g. As, Sb, Bi and others, may behave similarly and be subject to cleavage by a base such as C_2H_5MgBr.

Experimental

A dry nitrogen atmosphere, along with the usual precautions to exclude air and moisture, was used. A 100 ml, three-necked flask equipped with a thermometer, nitrogen inlet, a 50 ml addition funnel and stirred by a magnetic bar was used. GLC analyses were performed on a Hewlett Packard 5880 instrument using a methylsilicone capillary column, Supelco SPB-1, 15 m, 0.53 mm i.d., 0.10 μm film. GC separations were accomplished on a Hewlett Packard 5750 instrument using a methylphenylsilicone column, HP, OV-17, 10% on Chromosorb W (80–100 mesh), 6 ft., 0.125 in. i.d. Mass spectra were determined by chemical ionization or electron impact on a DuPont type 21-491 B instrument.

Reaction of tris(pentafluorophenyl)phosphine with ethylmagnesium bromide

Ethylmagnesium bromide (0.0125 mol, 12.5 ml of a 1.0 M THF solution) was rapidly added to an ice-cooled 0 °C THF solution (37 ml) of tris(pentafluorophenyl)phosphine [13] (6.0 g, 0.0113 mol) containing dodecane (0.50 g) as an internal standard. An exotherm of *c.* 14 °C was immediately observed as the solution turned purple. The reaction was stirred for 5 min during which time the temperature dropped to 1.0 °C. Carbon dioxide was then bubbled through the solution for 30 min. The addition of CO_2 caused an exotherm of *c.* 9 °C. After the addition of CO_2, the reaction mixture was treated with HCl (20 ml, 6 N) and diethyl ether (40 ml). The organic and aqueous layers were phase-separated. The aqueous layer was extracted with diethyl ether (50 ml) and the diethyl ether was added to the original organic layer. The combined layers were further extracted with NaOH (4 ×, 6 N) and phase-separated. The aqueous layer was neutralized with HCl (6 N) and extracted with diethyl ether, phase-separated and the dried ($MgSO_4$) organic layer was evaporated leaving a white solid (1.7 g, 71% yield). Recrystallization from hexane gave pentafluorobenzoic acid, m.p., 103–

104 °C (lit value [1]:103–104 °C) as a white solid. Its infrared spectrum was identical to that of a known sample of pentafluorobenzoic acid.

The organic layer remaining after NaOH extraction was dried ($MgSO_4$) and the organic solvents evaporated leaving 4.4 g of a yellow liquid. GC–MS analysis (GC area%) indicated the following peaks in ascending retention time: (A) $C_{14}H_5F_{10}P$ [$(C_6F_5)_2PC_2H_5$, 82%]; (B) $C_{12}F_9H$ (possibly $C_6F_5C_6F_4H$, 4%); (C) $C_{20}H_5F_{14}P$ (two isomers, probably $(C_6F_5)_2(C_2H_5C_6F_4)P$ and $(C_6F_5)(C_6F_5C_6F_4)PC_2H_5$, 4.5%); (D) $C_{18}F_{15}P$ (starting material, $(C_6F_5)_3P$, 7.8%) and trace amounts of $C_{16}H_5F_9P$, $C_{24}F_{19}P$ and two isomers of $C_{24}H_5F_{18}P$. Compound A was isolated using a preparative column. Its mass spectral analysis and infrared spectrum were identical to those of a known sample prepared as described below. Compound B [14] and D had GC retention times identical to known standards. Compounds C and all remaining trace compounds were not characterized further.

Reaction of bis(pentafluorophenyl)phosphorus bromide with ethylmagnesium bromide

Ethylmagnesium bromide (0.023 mol, 23 ml of a 1 M THF solution) was added dropwise to bis(pentafluorophenyl) phosphorus bromide (0.020 mol, 8.9 g) in THF (20 ml). A moderate exotherm was observed so that cooling with an ice bath was required. After *c.* 20 min necessary to complete the addition, a dark brown colored solution with a precipitate was observed. After an additional 20 min, the reaction mixture was treated with HCl (6 N) and diethyl ether added. The reaction was phase-separated, the organic layer washed additionally with H_2O (3×) and dried ($MgSO_4$). On evaporation of the solvent, 6.9 g of a residual liquid resulted. Fractional distillation gave the product $(C_6F_5)_2PC_2H_5$ (4.7 g, 59%), b.p., 97–98 °C/0.7 mmHg (lit. value [15]:b.p., 105–107 °C/0.4 mmHg). MS *m/e*:394 $(M)^+$; 365 $(M-19)^+$; 296 $(M-F_2PC_2H_5)^+$; 198 $(M-C_6F_5C_2H_5)^+$. IR (neat) cm^{-1}: 2960; 2915; 2870; 1630; 1505; 1480; 1460; 1380; 1280; 1080; 970; 830.

Reaction of bis(pentafluorophenyl)sulfide with ethylmagnesium bromide

Bis(pentafluorophenyl)sulfide [16] (4.0 g, 0.0109 mol), THF (20 ml) and n-dodecane (0.3 g, internal standard) were combined in the reaction flask which was then cooled to −6 °C (sodium chloride–ice water bath). Ethylmagnesium bromide (0.0109 mol of a 1.0M THF solution) was added dropwise over a 15 min period. An immediate exotherm of *c.* 10 °C was noted and the solution turned purple. The exotherm was limited by adjusting the rate of addition of ethylmagnesium bromide. After 5 min, a GC sample showed that 88% of $(C_6F_5)_2S$ was present. The reaction was stirred for an additional 7 h. Carbon dioxide was then bubbled through the solution for 30 min. The mixture was treated with 6 N HCl (30 ml) and diethyl ether (100 ml). The organic layer was phase-separated and extracted with NaOH solution and phase-separated again. The aqueous layer on acidification and extraction with diethyl ether produced no $C_6F_5CO_2H$. The original organic layer was dried ($MgSO_4$), filtered and the solvents evaporated to give 2.1 g of a liquid. GC–MS analysis of the liquid showed the following products (GC area%): (A) $C_8H_5F_5S$ ($C_2H_5SC_6F_5$, 35.3%); (B) $C_{12}F_{10}S$ ($C_6F_5SC_6F_5$, 15.4%); (C) $C_{14}H_5F_9S$ (two isomers, $C_6F_5SC_6F_4C_2H_5$ or $C_2H_5SC_6F_4C_6F_5$, 18.8%); (D) $C_{18}F_{14}S$ ($C_6F_5SC_6F_4C_6F_5$, 9.5%); (E) $C_{20}H_5F_{13}S$ ($C_2H_5C_6F_4SC_6F_4C_6F_5$, 5.1%); (F) $C_{24}F_{18}S$ (isomers, $C_6F_5C_6F_4SC_6F_4C_6F_5$ or $C_6F_5SC_6F_4C_6F_4C_6F_5$, 5.0%); (G) unidentified products.

Compound A was isolated on a preparative column and its infrared spectrum shown to be identical to that of a known standard sample [17]. The mass spectral analysis was consistent with the structure exhibiting the *m/e* values: 228 $(M)^+$, 209 $(M-19)^+$; 200 $(M-C_2H_4)^+$; 199 $(M-C_2H_5)^+$; 168 $(M-C_2H_4S)^+$; 167 $(M-C_2H_5S)$. Compound B had the same GC retention time as the starting material. All other minor products were partially identified by mass spectral analysis alone; hence their structures are tentative.

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