Journal of Fluorine Chemistry, 5 (1975) 475 – 480

Received: August 6, 1974

SHORT COMMUNICATION

Stability and Reactions of 1,6-Bis(Magnesium Bromide) Dodecafluorohexane

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We have recently reported [1] the synthesis of the first perfluoroaliphatic bis-Grignard reagent $BrMg(CF_2)_6MgBr$ (I). This bis-Grignard reagent can be conventiently synthesized through the metal-halogen exchange reaction.

$$Br(CF_2)_6BR + 2C_2H_5MgBr \longrightarrow 2C_2H_5Br + BrMg(CF_2)_6MgBr \qquad (1)$$

In our continuing studies on perfluoroaliphatic organometallic compounds, the thermal stability and utility of the bis-Grignard reagent as an intermediate for the synthesis of 1,6-substituted perfluorohexanes have been examined.

Perhaps the most stringent restriction placed on the use of perfluoroaliphatic mono-and di-Grignard reagents as synthesis intermediates is temperature [1, 2, 3, 4]. The success of a synthesis approach utilizing perfluoroaliphatic Grignard reagents depends on the selection of a reaction temperature at which the rate of reaction with a substrate is much greater than the rate of thermal decomposition. The bis-Grignard I undergoes only about 10% decomposition at -70° in THF over 18h. At -50° however, the same reagent exhibits a half-life of only 2h. Based on this data the reaction temperature selected for subsequent reactions was -70°. Unlike the thermal decomposition of other perfluoroaliphatic Grignard reagents [1, 2, 3, 4], the thermal decomposition of the bis-Grignard I was extremely facile affording perfluorocyclohexene (II) in 90% yield. Ring closure in the six

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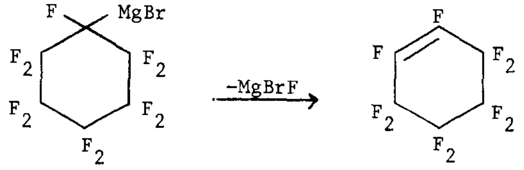
membered ring system is of course thermodynamically favorable. This coupled with the previous observations that perfluoroaliphatic Grignard addition to perfluoroolefins is fast could account for the formation of perfluorocyclohexene. One plausible mechanism in the thermal decomposition of I may involve the following.

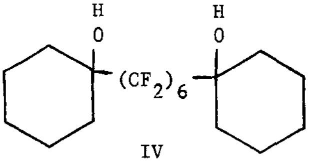
$$\mathrm{BrMg(CF_2)_6MgBr} \xrightarrow{-\mathrm{MgBrF}} \mathrm{F_2C{=}CF(CF_2)_4MgBr} \xrightarrow{\text{addition}}$$



(2)

The reaction of the bis-Grignard I with dilute aqueous acid to yield the 1,6-dihydro compound $H(CF_2)_6H$ and with CO_2 to yield the diacid $HO_2C(CF_2)_6CO_2H$ in high yields has been previously reported [1]. Further synthesis utility of I has been shown by reacting the organometallic with a variety of substrates. The reaction with $(CH_3)_3SiCl$ produced a 32% yield of $(CH_3)_3Si(CF_2)_6Si(CH_3)_3$ (III) * .

The reaction between I and cyclohexanone yielded the bis-alcohol IV (34%)



IV

The reaction between I and acetone yielded two principal products, the mono-alcohol $H(CF_2)_6C(CH_3)_2OH$ (V) (34%) and the bis-alcohol $HO(CH_3)_2C(CF_2)_6C(CH_3)_2OH$ (VI) (28%).

In the reactions of I with the trimethylchlorosilane, cyclohexanone and acetone, the rates of reaction at -70° appeared to be slow and undoubtedly are the reason for the low yields of products. In all these

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* This compound has been previously reported [5] in approximately 70% yield by the in-situ method.

instances perfluorocyclohexene the product of the competing decomposition reaction was detected in the reaction mixture. Higher yields of 1,6-disubstituted perfluorohexanes can be obtained by using more reactive substrates. Hexafluoroacetone for example, has been reported to react faster than acetone towards nucleophilic reagents [6]. Thus the reaction between the bis-Grignard I and hexafluoroacetone yielded the bis-perfluorotertiary alcohol, $HO(CF_3)_2C(CF_2)_6C(CF_3)_2OH$ (VII) in considerably higher yields (62%).

The availability of the bis-Grignard reagent I as well as the other alpha-omega bis-Grignard reagents previously reported [1] should now provide a convenient synthesis route to bis substituted perfluoroalkanes.

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded on a Varian A56/60 spectrometer in CCl_4 solution. Chemical shifts are expressed in ppm units using tetramethylsilane and fluorotrichloromethane as internal standards. GLC analysis were performed using a 1.8m, 10% SE-30 on Chromosorb W column, and a 3.6m, 10% Apiezon L on Chromosorb W. All products were characterized by GLC retention time with calibrated known samples. Yields of products were determined by GLC analysis using appropriate hydrocarbon internal standards.

Thermal decomposition of 1,6-bis(magnesium bromide) dodecafluorohexane

The bis-Grignard reagent I (4 mmol), prepared as described previously [1] from $Br(CF_2)_6Br$, and C_2H_5MgBr in THF, was stirred at -70° for 30 min and then allowed to warm rapidly to room temperature (~15 min). The reaction mixture was quenched with 20 ml of 6 N HCl, extracted with benzene (3 x 50 ml), and the combined benzene extracts dried ($MgSO_4$). Subsequent GLC analysis indicated a single decomposition product, perfluorocyclohexene (II) (90%). The product II was collected by preparative GLC. Its infrared spectrum and GLC retention time were identical with an authentic sample. The mass spectrum exhibited peaks at 262 (M), 243 (M-F), 131 (CF_2CF_2CF) and 69 (CF_3). ^{19}F NMR spectroscopy gave the following data: a quartet at 118 (4F, $\underline{CF_2}CF=$), $J(CF_2CF=)$5 Hz; a multiplet at 133(4F, $(\underline{CF_2})_2$; and a multiplet at 151 (2F, CF=CF).

Reaction of bis-Grignard I with $(CH_3)_3SiCl$

To a solution of the bis-Grignard I (4 mmol) in THF (100 ml) was added an excess of $(CH_3)_3SiCl$ (10 mmol). The reaction was stirred at -70° for 72h and then allowed to warm slowly to room temperature (30 min). GLC analysis after hydrolysis of the reaction indicated the disilane $(CH_3)_3Si(CF_2)_6Si(CH_3)_3$ (III) (32%) and perfluorocyclohexene. The disilane III had a GLC retention time and an infrared spectrum identical to an authentic sample kindly provided by Professor Henry Gilman [5].

Reaction of the bis-Grignard I with cyclohexanone

To the bis Grignard I (20 mmol) at -70° was added cyclohexanone (40 mmol) and the reaction was allowed to stir at -70° for 5h. The reaction was warmed slowly to room temperature and the solvent was removed at reduced pressure. The resulting solid was treated with excess 6N HCl, extracted with diethyl ether, the extracts dried ($MgSO_4$) and concentrated at reduced pressure. GLC analysis indicated one major and two minor products. The crude reaction mixture was subjected to silica gel column chromatography. Elution with 10% diethyl ether/n-pentane afforded a yellow oil which contained the two minor products. One of these products was subsequently isolated by GLC and analyzed by mass spectral analysis which displayed peaks at 381 (M-F), 99($C_6H_{10}OH$) and 69(CF_3). These limited data suggest the product to be the mono-substituted compound 1-cyclo-$C_6H_{10}OH(CF_2)_6H$ (M = 400). Further elution employing 20% diethyl ether/pentane, afforded a white solid (major product) (4.3g, 43% yield). The solid was sublimed at 60-70°/10^{-2}mm, m.p. 151-152°. The product was characterized as the bis-alcohol IV (nc). Analysis: Found: C, 43.51, H, 4.3%. $C_{18}F_{12}H_{22}O_2$ requires C, 43:37; H, 4.4%. Mass spectral analysis indicated peaks at 480(M-18), 99($C_6H_{10}OH$) and 69 (CF_3). ^1H NMR indicated the following: multiplet at 1.63 (20H, $C_6\underline{H}_{10}$) and a singlet at 3.58 (2H, O$\underline{H}$). ^{19}F NMR indicated the following: multiplet at 119.7(4F, $C_6H_{10}(OH)C\underline{F}_2$) and a multiplet at 123.0 (8F, $CF_2\underline{(CF_2)_4}CF_2$).

Reaction of bis-Grignard I with acetone

The reaction was performed as described above for cyclohexanone except that an excess of acetone (250%) was used and the reaction was stirred for 18h at -70°. The products were separated by GLC which indicated two components, $H(CF_2)_6C(CH_3)_2OH$ (V) (nc) and $HO(CH_3)_2C(CF_2)_6C(CH_3)_2OH$, m.p. 88-89° (VI)(nc). Analysis for V: Found: C, 29.2; H, 2.22%. $C_9F_{12}H_8O$ requires C, 30.0; H, 2.22%. Mass spectral analysis indicated peaks at 345 ($M-CH_3$) and 59 ($C(CH_3)_2OH$). ^{19}F NMR indicated the following: multiplet at 120.0 (2F, $\underline{CF_2}(CH_3)_2OH$) multiplet at 122.3 and 124.3 (6F, $(\underline{CF_2})_3$), multiplet at 130.6 (2F, $\underline{CF_2}CF_2H$) and a doublet of triplets at 138.0 (2F, $\underline{CF_2}H$). ^1H NMR indicated a singlet at 1.45 (6H, $\underline{CH_3}$), broad singlet at 3.13 (1H, $\underline{OH}$) and a triplet of triplets at 6.00 (1H, $CF_2\underline{H}$). Analysis for VI: Found: C, 34.4; H, 3.2%. $C_{12}F_{12}H_{14}O_2$ requires C, 34.4; H, 3.4%. Mass spectral analysis indicated peaks at 418 (M) and 59 ($(C(CH_3)_2OH$. ^{19}F NMR indicated the following: multiplet 120 (4F, $\underline{CF_2}C(CH_3)_2$) and a multiplet at 122 (8F, $(\underline{CF_2})_4$). ^1H NMR indicated a singlet at 1.17 (12H, CH_3) and a broad singlet at 1.43 (2H, $\underline{OH}$).

Reaction of bis-Grignard I with hexafluoroacetone

The reaction was performed as described above for cyclohexanone except that an excess of hexafluoroacetone (100%) was used and the reaction was stirred for 18h at -70°. GLC analysis indicated two reaction products, major $HO(CF_3)_2C(CF_2)_6C(CF_3)_2OH$ (VII) (nc) 62% yield and a minor component $H(CF_2)_6C(CF_3)_2OH$ (VIII) (nc). Analysis of VII: Found: C, 22.3; H, 0.30%. $C_{12}F_{24}H_2O_2$ requires C, 22.7; H, 0.32%. Mass spectral analysis indicated a peak at 634 (M). ^{19}F NMR indicated the following: multiplet at 73.2 (12F, $C(\underline{CF_3})_2OH$), multiplet at 116 (4F, $\underline{CF_2}(CF_3)_2OH$), multiplet at 121 (8F, $(\underline{CF_2})_4$). ^1H NMR indicated a broad peak at 3.7 ($(C(CF_3)_2\underline{OH}$. Analysis of VIII: Found: C, 22.8; H, 0.47%. $C_9F_{18}H_2O$ requires C, 23.1; H, 0.43%. Mass spectral analysis indicated a peak at 468 (M), 448 (M-HF) and 431 (M-HF-OH). ^{19}F NMR indicated the following: multiplet 73.2 (6F, $C(\underline{CF_3})_2OH$), multiplet 115 (2F, $\underline{CF_2}C(CF_3)_2OH$), multiplet 121, 122, 124 (6F, $(\underline{CF_2})_3$), multiplet 130 (2F, $\underline{CF_2}CF_2H$) and multiplet at 138 (2F, $\underline{CF_2}H$). ^1H NMR indicated a broad peak at 3.7 ($(CF_3)_2\underline{OH}$) and a triplet of triplets at 6.0 ($CF_2\underline{H}$).

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