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

PREPARATION OF α,ω-BIS(DIMETHYLHYDROSILYL)PERFLUOROHEXANE

MILTON R. SMITH JR. AND HENRY GILMAN
Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U. S. A.)

(Received May 6th, 1972)

SUMMARY

The *in situ* reaction of α,ω-dibromoperfluorohexane, magnesium and chlorodimethylhydrosilane has been optimized on a small-scale. These conditions were scaled-up and used to prepare α,ω-bis(dimethylhydrosilyl)perfluorohexane in good yields.

INTRODUCTION

As part of a study on perfluoroalkylsilanes, and particularly the important α,ω-disubstituted perfluoroalkanes[1], we wished to obtain α,ω-bis(dimethylhydrosilyl)-perfluorohexane. A route to this compound appeared to be the *in situ* reaction of α,ω-dibromoperfluorohexane, magnesium and chlorodimethylhydrosilane.

The *in situ* reaction of α,ω-dibromoperfluorohexane, magnesium (or *more particularly* lithium) and chlorotrimethylsilane in THF produced α,ω-bis(trimethylsilyl)perfluorohexane in good yield[1]. A similar reaction with 1,4-dibromoperfluorobutane had also given the corresponding silane in satisfactory yield[1]. Prior to this, only one other report in the literature had involved a transient α,ω-dimetalloperfluoroalkane[2].

RESULTS AND DISCUSSION

We have concentrated our efforts on the use of magnesium largely because of a secondary reaction between lithium and chlorohydrosilanes[3]. It was also previously observed[4] that the further reaction of perfluorinated derivatives to give allenes was substantially reduced when magnesium was used in place of lithium with *in situ* reactions.

Initially the optimal conditions were determined from the small scale [2.5 mmole of $Br(CF_2)_6Br$] experiments. The solvent, the ratio of $Br(CF_2)_6Br$/magnesium/chlorodimethylhydrosilane and the temperature were important factors. The thorough drying of the glassware also has a significant effect.

The single reaction which was attempted in ether showed this solvent to be ineffective. THF was found to be convenient and effective. No attempt was made to investigate other solvents at this time.

The ratio of reactants was one of the more critical factors in improving the yield of $HMe_2Si(CF_2)_6SiMe_2H$ (I). An excess of magnesium was beneficial but more important was an excess of the chlorohydrosilane. We have found a ratio of $Br(CF_2)_6Br/Mg/ClSiMe_2H$ of 1/3/10 to be satisfactory. Increasing the amount of Mg or $ClSiMe_2H$ did not improve the yield.

The temperature as long as it was between ca. −10 and −50° seemed to have little effect on the yields. Lower temperature (−78°) caused the reaction to be sluggish. Starting the reaction at −40° to −20° and then allowing the mixture to warm slowly (36-48 h) to 25° gave good results (92–94% yield). The dryness of the glassware has a measurable effect. It was found that for consistency and high yield, glassware should be dried at 120° for 24 h.

When the reaction was scaled up, a concentration effect was noticed. The yields were 10-15% higher when 120-125 ml THF was used (as contrasted with 200 ml). The relatively large hold-up (0.8 g) of material on the spinning band column significantly reduces the isolated yield of $HSiMe_2(CF_2)_6SiMe_2H$.

This *in situ* reaction can be visualized as going through a mono- or di-Grignard intermediate. Perfluoroalkylmetallic reagents are known to decompose via the β-elimination reaction[5,6]. This latter reaction will be minimized by factors which decrease the half-life of the intermediate organometallic compound. Such factors were observed to be lower temperature, increase in concentration of reagents and a large excess of the derivatizing reagent ($ClSiMe_2H$).

The ^{19}F NMR spectra of $Br(CF_2)_6Br$ and $HMe_2Si(CF_2)_6SiMe_2H$ were predictably simple, although assignment of each multiplet to definite $-CF_2-$ groups is not possible at this time.

The α,ω-bis(dimethylhydrosilyl)perfluoroalkanes are readily converted by RLi compounds to the corresponding α,ω-dilithioperfluoroalkanes. In like manner, the corresponding $XMg(CF_2)_nMgX$ types are formed: (1) by reaction of the α,ω-bis(dimethylhydrosilyl)perfluoroalkanes with Grignard reagents; and (2) by halogen–metal exchange of $Br(CF_2)_nBr$ with RMgX compounds; and (3) by reaction of $Li(CF_2)_nLi$ with magnesium halides. Related reactions can be used for the synthesis of some other $M-(CF_2)_n-M$ types.

EXPERIMENTAL

All reactions were effected under an atmosphere of dry oxygen-free nitrogen. Glassware was dried at 120°, assembled while hot, and flushed with dry nitrogen while cooling. Tetrahydrofuran (THF) was dried over sodium and distilled from sodium benzophenone ketyl. Chlorodimethylsilane was from the Dow Corning Corporation and was used as received. Magnesium turnings were from the Mallinkrodt Chemical Works. α,ω-Dibromoperfluorohexane (Du Pont and Dow Corning) was used without further purification. The IR spectra were taken as thin films on NaCl plates with a Perkin Elmer Model 21 spectrophotometer. ^1H NMR spectra were of CCl_4 solutions (20%) on a Varian A-60. ^{19}F NMR spectra were of the neat liquids using $CFCl_3$ as the internal standard, and were recorded on a Varian HR-60 spectrometer. VPC analyses were made on an F & M Model 500 Gas Chromatograph using a $4\frac{1}{2}' \times \frac{1}{4}''$ column packed with Silicone Gum Rubber (15% on Chromosorb W) at 110°. Weighed mixtures of n-$C_{12}H_{26}$ and $Me_2HSi(CF_2)_6SiMe_2H$ (I) were injected in the VPC and a plot of the wt. ratio *vs.* the area ratio of (I)/n-$C_{12}H_{26}$ was used to determine the yields from the small-scale experiments.

Small-scale in situ reactions

The following optimal ratio and conditions will serve to illustrate the procedure.

To a 250 ml three-necked flask was added Mg (0.182 g, 7.5 mg-atom), 35 ml THF and 0.75 g n-$C_{12}H_{26}$ (VPC internal standard). This mixture was cooled to $-20°$ and a mixture of $Br(CF_2)_6Br$ (1.15 g, 2.5 mmole) and $ClSi(CH_3)_2H$ (2.35 g, 25 mmole) was added. Samples withdrawn at various times and analyzed by VPC showed the following yields: after 4.5 h, 58%; 12 h, 68%; and 24 h, 68%. The mixture was then allowed to warm to room temperature and was stirred for an additional 48 h. The yield was 94% based on the initial amount of $Br(CF_2)_6Br$. After some difficulties in getting reproducible yields it was discovered that drying of glassware for at least 24 h at 120° was necessary in order to give high and consistent yields. In a separate experiment, with the same amounts of reactants, the mixture was warmed from $-20°$ to 25° during 36 h to give a 92% yield of (I).

Preparation of $H(CH_3)_2Si(CF_2)_6Si(CH_3)_2H$; larger scale in situ reactions

To a 250 ml three-necked flask equipped with a stirrer and a nitrogen inlet was added Mg (1.46 g, 0.06 g-atom) and 120 ml THF. This was cooled to $-40°$, and to the flask was added a mixture of $Br(CF_2)_6Br$ (9.2 g, 0.02 mole) and $ClSi(CH_3)_2H$ (18.8 g, 0.20 mole). The mixture was stirred for ca. 12 h at -35 to $-40°$, then allowed (during 30 h) to warm to room temperature and stirred for an additional 8 h. To the reaction mixture was added ca. 200 ml of dry pet. ether (b.p. 60-70°) and this was then extracted with ca. 100 ml of 3 *N* HCl (to remove Mg salts). The organic layer was separated, dried with Na_2SO_4, and the solvents distilled under nitrogen through a $10'' \times 1''$ glass helix-packed column. The crude $H(CH_3)_2Si(CF_2)_6Si(CH_3)_2H$ (I) was then distilled on a spinning-band column. Two fractions were collected: (1) 0.7 g, b.p. 60-70°/1.8 mm [92% (I) and ca. 8% $Br(CF_2)_6Br$ by VPC]; and (2) 5.75 g, (69% yield), b.p. 70-72°/1.8 mm (98% pure by VPC). A portion (2.0 g) of fraction (2) was redistilled to give an analytical sample. (Found: C, 28.68; H, 3.47. $C_{10}H_{14}F_{12}Si_2$ calcd.: C, 28.71; H, 3.37%.). The ^1H NMR (CCl_4 solution) showed a broad multiplet at 5.8 ppm (SiH), and a doublet at 9.62 ppm [$Si(CH_3)_2$] integrating for 1 and 6 protons, respectively. The IR (neat on NaCl plates) showed an absorption at 2190 cm^{-1} (Si–H), strong bands between 1100–1300 cm^{-1} (C–F) and at 845, 875 and 895 cm^{-1} [$Si(CH_3)_2$]. The above reaction was repeated several times. Yields ranged from 66-69%.

The ^{19}F NMR spectrum showed three multiplets at 120, 121 and 127 ppm (relative to $CFCl_3$ on the ϕ scale). Integration showed these to be in the ratio of 1/1/1. The ^{19}F NMR spectrum of $Br(CF_2)_6Br$ was taken for comparison. It shows three multiplets of equal intensity at 63, 117 and 121 ppm, respectively.

ACKNOWLEDGEMENT

This research was supported in part by the United States Air Force under Contract No. F33615-69-C-1046 monitored by the Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio; as well as by the National Science Foundation (GP-34632). We are grateful to the Du Pont Co. for part of the $Br(CF_2)_6Br$ used; and to Mr. Norbert Morales for the ^{19}F NMR spectra.

REFERENCES

1 A. E. Jukes and H. Gilman, *J. Organometal. Chem.*, 18 (1969) P33.
2 P. Johncock, *J. Organometal. Chem.*, 6 (1966) 433.
3 H. Gilman, K. Shiina, D. Aoki, B. J. Gaj, D. Wittenberg and T. Brennan, *J. Organometal. Chem.*, 13 (1968) 323.
4 D. H. Ballard and H. Gilman. *J. Organometal. Chem.*, 19 (1969) 199.
5 E. S. Lo, *J. Org. Chem.*, 36 (1971) 364.
6 W. A. Sheppard and C. M. Sharts, *Organic Fluorine Chemistry*, Benjamin, New York, 1969.