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

PRELIMINARY COMMUNICATION

REACTION OF SOME α, ω-DIBROMOPERFLUOROALKANES WITH LITHIUM AND MAGNESIUM

A.E. JUKES and H. GILMAN
Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U.S.A.)

(Received July 7th, 1969)

We have been interested in the preparation of some α, ω-dimetalated perfluoroalkanes, $M(CF_2)_nM$, from the α, ω-dibromoperfluoroalkanes, $Br(CF_2)_nBr$, rather than the corresponding diiodides. Few dimetalated perfluoroalkanes have been reported. Among those known are the highly unstable 1,4-dilithiooctafluorobutane[1], the very stable, 1,3-dicopperhexafluoropropane[2], and probably some di-Grignard reagents[3]. All have been prepared from the highly expensive and relatively inaccessible diiodides.

Very little is known about the reaction of perfluoroalkyl *bromides* with various metals such as lithium, magnesium, zinc and copper. Perfluoro-n-propyl bromide reacted, very slowly, with zinc dust[4], and also with magnesium in ether[5] as addition of water gave 1-H-heptafluoropropane. McBee *et al.*[6] found that trifluoromethyl bromide did not react with sublimed magnesium in ether, but partially reacted with a mixture of magnesium and mercury. Reactions of unspecified perfluoro-alkyl and or -cycloalkyl bromides with magnesium were mentioned[7], but no details have appeared. We have found that 1,2-dibromotetrafluoroethane, 1,2-dibromohexafluoropropane, and 2,3,3-trichloroheptafluorobutane react with magnesium in THF at the ambient temperature, with elimination of magnesium halides and formation of olefins. However, 1,4-dibromooctafluorobutane and 1,6-dibromododecafluorohexane did not react with magnesium under similar conditions With magnesium activated by stirring dry in an atmosphere of nitrogen[8], a reaction did occur, even at low temperature, and we have obtained evidence indicating the formation of a di-Grignard reagent. Most significantly, an *in situ* reaction of both the dibromobutane and the dibromohexane with magnesium and chlorotrimethylsilane in THF at *ca.* -50°, afforded 45–50% yields of the respective α, ω-bis(trimethylsilyl)perfluoroalkanes. 1,4-Bis(trimethylsilyl)octafluorobutane is a solid, m.p. 28–29°; while 1,6-bis(trimethylsilyl)dodecafluorohexane is a liquid, b.p. 116°/15 mm, MR_D obs. 78.08, MR_D calc. 78.1. The IR spectra of both compounds show absorptions associated with the trimethylsilyl group and the perfluoroalkyl chain.

Similar *in situ* reactions were carried out with lithium and chlorotrimethylsilane in THF at low temperatures. 1,6-Bis(trimethylsilyl)dodecafluorohexane was obtained in a yield of 65.5% at -70° to -50°, the yield decreasing with increasing temperature. At -30° the yield was only 45% and 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-tetraene[9] and tetrakis-(trimethylsilyl)allene[10] were formed as by-products in low yields. Polysilylations of some polyfluorinated alkanes have been reported recently[11]. We have obtained no evidence, as yet, for the formation of any intermediate dilithioperfluoroalkanes in these reactions as the α, ω-dibromoperfluoroalkanes have, so far, not reacted with only lithium metal.

To the best of our knowledge, no direct attempted reaction of a perfluoroalkyl bromide with lithium has been reported. Only one report of a reaction between a perfluoroalkyl iodide and lithium has come to our notice[12]. Reaction of perfluoro-n-propyl iodide with lithium and benzaldehyde[12] afforded a very low yield of the desired product, although higher product yields were obtained in *in situ* reactions of perfluoro-n-propyl iodide with lithium and chlorosilanes[13].

ACKNOWLEDGEMENT

This research was supported by the United States Air Force, under Contract F33615-69-C-1046 monitored by Material Laboratories, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

REFERENCES

1 P. Johncock, *J. Organometal. Chem.*, 6 (1966) 433.
2 V.C.R. McLaughlin, J. Thrower and I.M. White, *4th International Symposium on Fluorine Chemistry*, Estes Park, Colorado (U.S.A.), July 24–28, 1967.
3 R.N. Haszeldine, *Nature*, 168 (1951) 1028.
4 W.T. Miller, Jr., E. Bergman and A.H. Fainberg, *J. Amer. Chem. Soc.*, 79 (1957) 4159.
5 T.J. Brice, W.H. Pearlson and J.H. Simons, *J. Amer. Chem. Soc.*, 68 (1946) 968.
6 E.T. McBee, R.D. Battershell and H.P. Braendlin, *J. Org. Chem.*, 28 (1963) 1131.
7 R.N. Haszeldine, *J. Chem. Soc.*, (1952) 3423.
8 A. Mendel, *J. Organometal. Chem.*, 6 (1966) 97.
9 T. Brennan and H. Gilman, *J. Organometal. Chem.*, 11 (1968) 625.
10 R. West, P.A. Carney and I.C. Mineo, *J. Amer. Chem. Soc.*, 87 (1965) 3788. See also, D.H. Ballard and H. Gilman, *J. Organometal. Chem.*, 14 (1968) 87 and preceding papers in this series.
11 D.H. Ballard and H. Gilman, *J. Organometal. Chem.*, 19 (1969) in press.
12 J.A. Beel, H.C. Clark and D. Whyman, *J. Chem. Soc.*, (1962) 4423.
13 H.C. Clark and D. Whyman, *2nd Int. Symposium on Fluorine Chemistry*, Estes Park, Colorado (U.S.A.), 1962, *Proceedings* p.232.