

Preliminary Note

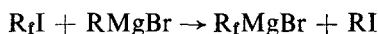
A novel preparation of *trans*-1-bromoperfluorovinyl compounds

RICHARD D. HOWELLS AND HENRY GILMAN

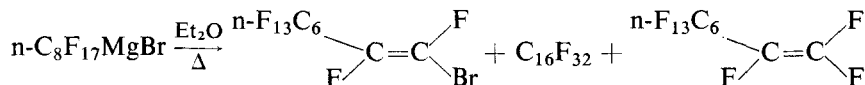
Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U.S.A.)

(Received September 26, 1973)

When perfluoroalkyl iodides are reacted with an alkyl- or aryl-magnesium bromide, a quantitative or nearly quantitative exchange takes place¹⁻⁶:



We have found that the major product from the slow thermal decomposition of R_fMgBr in ether or pentane (Skelly A) solvents is a *trans*-1-bromoperfluorovinyl compound.



For example, the products of decomposition of the perfluoro-octylmagnesium bromide are the *trans*-1-bromoperfluorovinyl compound (50-60%), the terminal perfluoro-olefin (*ca.* 10%), an internal olefin of molecular formula $C_{16}F_{32}$ (*ca.* 20%) and several very minor unidentified products including a compound presumed to be a *trans*-1-alkylperfluorovinyl compound (*ca.* 1-4%). The reaction appears to be general for perfluoroalkylmagnesium bromides obtained from $n-C_6F_{13}I$, $n-C_8F_{17}I$ and $n-C_{10}F_{21}I$.

The slow thermal decomposition of the corresponding perfluoroalkylmagnesium iodides results in formation of the *trans*-1-iodoperfluorovinyl compounds which are isolated in significantly lower yields than the bromo-substituted olefins obtained from the perfluoroalkylmagnesium bromides. Presumably this is due to the less favorable equilibrium involved in the formation of the perfluoroalkylmagnesium iodide.



Slightly higher isolated yields of the *trans*-1-bromoperfluorovinyl compounds (*ca.* 50%) were obtained when $MeMgBr$ was employed for the halogen-metal exchange instead of $EtMgBr$. A typical procedure involved addition of $EtMgBr$ (0.021 mol) to a stirred solution (slurry at $-78^\circ C$) of $n-C_8F_{17}I$ (0.020 mol) in *ca.* 125 cm³ of anhydrous ether. After 0.5 h at $-78^\circ C$, the reaction mixture was allowed to warm slowly (1-6 h) to room temperature. Magnesium salts were removed by washing with 2.0 mol l⁻¹ HCl followed by several washings with water. Distillation of the reaction mixture provided 4.35 g (47%) of *ca.* 96% pure *trans*-

1-bromopentadecafluoro-oct-1-ene, b.p. 78–80 °C / 92 mmHg. Preparative GLC (SE-30) provided an analytically pure sample, b.p. 140 °C (micro); n_D^{25} 1.3215; IR (neat): $\nu(\text{C}=\text{C})$ 1710 cm^{-1} and $\nu(\text{C}-\text{F})$ 1100–1400 cm^{-1} ; ^{19}F NMR (in CCl_4) $[\text{R}_f\text{CF}_2]_{\text{F}_b}\text{C}=\text{C}[\text{F}_a]_{\text{Br}}$: -105.7 ppm [dtt, $J(\text{F}_a, \text{F}_b) = 141$ Hz, $J(\text{F}_a, \text{CF}_2) = 26$ Hz, $J(\text{F}_a, \text{CF}_2\text{CF}_2\text{R}_f) = 5$ Hz, F_a], -154.0 ppm (dm, F_b), -81.7 ppm (t, CF_3), and broad multiplets at -117.6 ($-\text{CF}_2-\text{C}=\text{C}-$), -122.9 (CF_2), -123.5 (CF_2), -124.2 (CF_2) and -126.9 ppm (CF_3CF_2-). The mass spectrum confirmed the presence of one bromine atom with parent ions of equal intensity at m/e 460 and 462 (mol. wt. 461), and base peaks of equal intensity at m/e 191 and 193 ($\text{C}_3\text{F}_4\text{Br}^+$). Analysis: Found: C, 20.10, 20.80; Br, 17.51%. $\text{C}_8\text{F}_{15}\text{Br}$ requires C, 20.84; Br, 17.34%. The only compounds of the type $\text{R}_f(\text{CF}_2)_n]_{\text{F}}\text{C}=\text{C}[\text{F} \text{ Br(I)}$ reported⁷ are those with $\text{R}_f = \text{CF}_3$, $n = 0$. Our procedure provides a convenient route to compounds whose metallic derivatives have much synthetic utility. We are currently examining reactions of the Grignard and lithium reagents which may be obtained in high yield from the *trans*-1-bromoperfluorovinyl compounds.

Results have been reported for perfluoroisopropylmagnesium bromide which gave perfluoropropene (70.5%)⁴ and for perfluoropropylmagnesium iodide which gave heptafluoropropane (76%) and perfluoropropene (6%)⁸.

Support of this research by the National Science Foundation (GP-34632) is gratefully acknowledged. We also thank Dr. R. H. Gobran and Dr. F. J. Marshall for assistance.

REFERENCES

- 1 O. R. PIERCE, A. F. MEINERS AND E. T. MCBEE, *J. Amer. Chem. Soc.*, **75** (1953) 2516.
- 2 E. T. MCBEE, A. F. MEINERS AND C. W. ROBERTS, *Proc. Indiana Acad. Sci.*, **64** (1955) 112; A. F. MEINERS, *Ph. D. Thesis*, Purdue University, Purdue, Indiana, 1956.
- 3 E. T. MCBEE, C. W. ROBERTS AND A. F. MEINERS, *J. Amer. Chem. Soc.*, **79** (1957) 335.
- 4 R. D. CHAMBERS, W. K. R. MUSGRAVE AND J. SAVORY, *J. Chem. Soc.*, (1962) 1993.
- 5 M. R. SMITH, JR., D. S. SETHI, B. B. SINGH AND H. GILMAN, unpublished studies.
- 6 M. R. SMITH, JR. AND H. GILMAN, *J. Organometal. Chem.*, **46** (1972) 251.
- 7 M. G. BARLOW, *Chem. Commun.*, (1966) 703.
- 8 R. N. HASZELDINE, *J. Chem. Soc.*, (1952) 3423.