Grignard Reagents from 1-Bromo-perfluoro-olefins. Reactivity of Perfluorinated Grignard Reagents

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Summary The synthesis and some examples of the reactivity of Grignard reagents obtained from 1-bromo-perfluoro-olefins, R_F–CF=CF–Br are reported; these intermediates lead to new perfluorinated carboxylic acids.

PERFLUOROALIPHATIC Grignard reagents, R_FMgBr have been synthesised only with difficulty and in poor yields,[1] and their use as synthetic intermediates has been limited.[2] However, recent papers have reported that they could be obtained in excellent yields using metal-halogen exchange reactions, and thus could be used as intermediates in the synthesis of various perfluorinated compounds.[3] The main product of the thermal decomposition of a perfluoroalkyl Grignard reagent was found to be a *trans*-1-halo-perfluoroalk-1-ene [equation (1)].

We now report the synthesis and some examples of the reactivity of the Grignard reagents obtained from these bromo perfluoro-olefins.

trans-1-Bromo-perfluoro-oct-1-ene (major product of the thermal decomposition of perfluoro-octylmagnesium bromide $C_8F_{17}MgBr$) reacted with elemental magnesium, at room temperature, in tetrahydrofuran, to give the corresponding Grignard reagent (**4**).

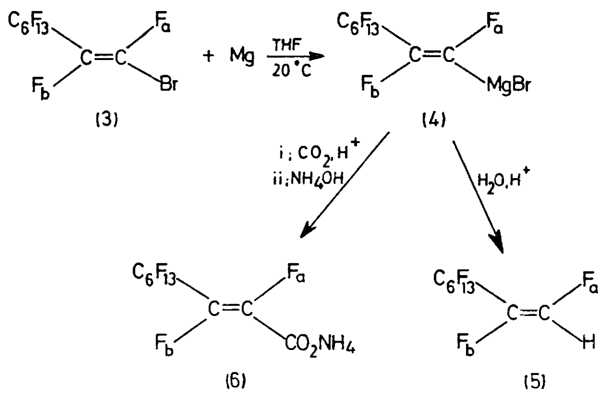
$$\underset{(1)}{R_F\text{-}CF_2\text{-}CF_2\text{-}I} \xrightarrow[Et_2O]{PhMgBr} \underset{(2)}{R_F\text{-}CF_2\text{-}CF_2\text{-}MgBr} \xrightarrow[Et_2O]{heat} \underset{(3)}{R_F\text{-}CF{=}CF\text{-}Br}$$

The reaction was easy in tetrahydrofuran, but did not occur in diethyl ether; this behaviour is similar to that observed with the hydrocarbon analogues.[4]

Metal-halogen exchange reactions between the bromo-perfluoro-olefin (**3**) and alkyl- or aryl-magnesium halides were attempted, but, in contrast to the saturated perfluoro-aliphatic Grignard reagents, no reaction was then observed.

The formation of the perfluoroalkylperfluorovinyl Grignard intermediate (**4**) was supported by its hydrolysis leading to the 1-hydro-perfluoro-oct-1-ene (**5**) and its reaction with CO_2, followed by a basic treatment, to give the ammonium salt (**6**) of the corresponding perfluorocarboxylic acid. [(**5**), b.p. (760 mmHg) 97—98 °C, yield = 60%; ^{19}F n.m.r. (ref. $CFCl_3$), δ_{F_a} 165·9, δ_{F_b} 178·9, J_{F_a,F_b} 135·5 Hz, $J_{F_a,H}$ 67·7 Hz; ^1H n.m.r. (ref. Me_4Si), δ_H 7·2, $J_{F_a,H}$ 70·0 Hz, $J_{F_b,H}$ 5·0 Hz; m/e = 382 (M), 363 (M − F); (**6**), m.p. 177°C (sublimation, or recrystallization from ethyl acetate); ^{19}F n.m.r. (acetone, ref. $CFCl_3$), δ_{F_a} 138·9, δ_{F_b} 160·7, J_{F_a,F_b} 142·0 Hz; m/e = 426 (M − NH_3), 381 (M − CO_2H); yield = 30%].

From ^{19}F n.m.r. studies, it could be shown that the *trans*-configuration of the vinylic fluorine atoms of the bromo-olefin (**3**) was maintained in the compounds (**5**) and (**6**). Therefore, the formation and reactions of perfluorinated vinylic Grignard reagents proceed with stereochemical integrity, similar to their hydrocarbon analogues.[4]



Scheme

These first examples of reactions of perfluoroalkylperfluorovinyl Grignard reagents, R_F-CF=CF-MgBr and those of the trifluorovinyl Grignard, CF_2=CF-MgX,[5] are in good agreement. The preliminary results indicate that perfluoroaliphatic Grignard reagents, saturated or unsaturated, can be considered as useful intermediates, from which it is hoped to extend a chemistry similar to that of the hydrocarbon analogues. The succession of two Grignard reactions in a series of perfluorinated compounds leads to a route for the synthesis of new 'heavy' perfluoroalk-2-ene 1-carboxylic acids, R_F–CF=CF–CO_2H.

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