ABSTRACT

Grignard Synthesis of Perfluoroalkyl-substituted

Phosphorus and Sulfur Compounds.

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Reactions between perfluoroalkyl Grignards, R_fMgX (where $R_f = C_nF_{2n+1}$, n = 1, 2, 3, 4, 6 and 8; X = Cl, Br), and selected main group halides were investigated. New routes towards the synthesis of perfluoroalkylphosphonic acids, $R_fPO_3H_2$, perfluoroalkylphosphonous acids, $R_fP(H)O_2H$, bis(perfluoroalkyl)phosphinic acids, $(R_f)_2PO_2H$, phenylbis(perfluoroalkyl) phosphine oxides, $OPPh(R_f)_2$, phenylperfluoroalkylphosphinic acids, $OPPh(R_f)OH$ and bis(perfluoroalkyl)sulfones, $(R_f)_2SO$, were developed. The acids were conveniently isolated as arylammonium salts by reaction with either aniline or *p*-toluidine.

R_fMgX reacts with OPX_3 (X = Cl, Br), $OPPhCl_2$ or $SOCl_2$ to afford exclusively, the di-substituted products, $(R_f)_2P(O)X$ (in situ), $OPPh(R_f)_2$ and $(R_f)_2SO$ respectively in good yields. Hydrolysis of $(R_f)_2P(O)X$ gives $(R_f)_2PO_2H$, while $OPPh(R_f)_2$ hydrolyses to yield $OPPh(R_f)OH$.

Grignard treatment of PX_3 gives both mono- and di-substituted products, R_fPX_2 and $(R_f)_2PX$ in good yields (in situ). The reaction conditions can be controlled to exclusively result in mono-substitution. Hydrolysis of R_fPX_2 gives $R_fPH(O)OH$, which upon oxidation, affords $R_fPO_3H_2$. The crystal structures of the phosphonic acid salts, $[p\text{–}CH_3C_6H_4NH_3]_2[C_2F_5PO_3]$ and $[p\text{-}CH_3C_6H_4NH_3][C_8F_{17}P(OH)O_2]$ are reported. The oxidative hydrolysis of $(R_f)_2PX$ serves as another route towards synthesizing $(R_f)_2PO_2H$.

Pefluoroalkyl Grignard treatment of other main group halides (such as BCl_3, $BiCl_3$, $SiBr_4$, Me_3SiCl, AsI_3, SO_2Cl_2 and $SeOCl_2$) was also tested. However, perfluoroalkyl-substituted products of these substrates were not observed under the conditions employed.

Keywords: Adil Imran Hosein, perfluoroalkyl, Grignard, phosphonic, acids, phosphonous, phosphinic, phosphine oxides, sulfones, hydrolysis, main group halides.