ABSTRACT

Grignard Synthesis of Perfluoroalkyl-substituted Phosphorus and Sulfur Compounds.

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Reactions between perfluoroalkyl Grignards, RfMgX (where Rf = CnF2n+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, RfPO3H2, perfluoroalkylphosphonous acids, RfP(H)O2H,
bis(perfluoroalkyl)phosphinic acids, (Rf)2PO2H, phenylbis(perfluoroalkyl) phosphine oxides, OPPh(Rf)2, phenylperfluoroalkylphosphinic acids, OPPh(Rf)OH and bis(perfluoroalkyl)sulfones, (Rf)2SO, were developed. The acids were conveniently isolated as arylammonium salts by reaction with either aniline or p-toluidine.

RfMgX reacts with OPX3 (X = Cl, Br), OPPhCl2 or SOCl2 to afford exclusively, the di-substituted products, (Rf)2P(O)X (in situ), OPPh(Rf)2 and (Rf)2SO respectively in good yields. Hydrolysis of (Rf)2P(O)X gives (Rf)2PO2H, while OPPh(Rf)2 hydrolyses to yield OPPh(Rf)OH.
Grignard treatment of PX₃ gives both mono- and di-substituted products, RₓPX₂ and (Rₓ)₂PX in good yields (in situ). The reaction conditions can be controlled to exclusively result in mono-substitution. Hydrolysis of RₓPX₂ gives RₓPH(O)OH, which upon oxidation, affords RₓPO₃H₂. The crystal structures of the phosphonic acid salts, [p−CH₃C₆H₄NH₃]₂[C₂F₅PO₃] and [p−CH₃C₆H₄NH₃][C₈F₁₇P(OH)O₂] are reported. The oxidative hydrolysis of (Rₓ)₂PX serves as another route towards synthesizing (Rₓ)₂PO₂H.

Perfluoroalkyl Grignard treatment of other main group halides (such as BCl₃, BiCl₃, SiBr₄, Me₃SiCl, AsI₃, SO₂Cl₂ and SeOCl₂) 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.