

A New Synthetic Route to Perfluoroalkylphosphonates involving Facile Formation of the CF–P Linkage

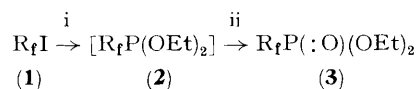
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Summary A new synthetic route to perfluoroalkylphosphonates which involves the facile formation of CF–P bonds is reported.

THE synthesis of organophosphorus compounds, at some stage, necessarily involves the formation of carbon–phosphorus linkages. The best known method of forming these linkages is by the Arbuzov reaction¹ which was originally formulated as a reaction between a trialkyl phosphite and an alkyl halide. Unfortunately this approach is not of general applicability to the preparation of the perfluoroalkylphosphonates. Exceptionally, some fluoromethyl halides have been reported to react with triethyl phosphite. CF₂Br₂ (thermally)² and CF₃I (photochemically)³ give the corresponding fluorinated methylphosphonates. Perfluoroalkyl iodides also react with white phosphorus at elevated temperature to form CF–P bonds.^{4,5}

We now report a facile formation of the CF–P linkage using tetraethyl pyrophosphite and the synthesis of diethyl perfluoroalkylphosphonates from corresponding perfluoroalkyl iodides *via* phosphonites (Scheme). In a typical



SCHEME. *Reagents*: i, [(EtO)₂P]₂O, Bu^tOOBu^t and CF₂CICFCl₂; ii, Bu^tOOH and MeOH–CF₂CICFCl₂.

procedure, a mixture of perfluoro-n-hexyl iodide (**1a**) (50.0 mmol) and tetraethyl pyrophosphite (75.0 mmol) in 1,1,2-trichloro-1,2,2-trifluoroethane (110 ml) with di-t-butylperoxide (25.0 mmol) was heated at 120 °C for 3 h in an

TABLE. Preparation of diethyl perfluoroalkylphosphonates (3).^a

Phosphonate	R _f	B.p./°C (<i>p</i> /mmHg)	Yield ^b /%
(3a)	n-C ₆ F ₁₃	58—60 (1.5)	71
(3b)	n-C ₄ F ₉	52—53 (7)	65
(3c)	iso-C ₃ F ₇	70—72 (21)	40

^a The ¹H, ¹³C, ¹⁹F, and ³¹P n.m.r. and the mass spectra were consistent with the assigned structures. Satisfactory elemental analyses were obtained for all compounds reported herein.

^b Isolated yield based on R_fI.

autoclave. The ¹⁹F and ³¹P n.m.r. spectra,† and g.l.c.-m.s. results demonstrated the formation of diethyl perfluoro-n-hexylphosphonite (2a) as the main product. Smooth

oxidation of (2a) at -10 to -5 °C with a solution of t-butyl hydroperoxide (180 mmol) in methanol (60 ml) under nitrogen gave diethyl perfluoro-n-hexylphosphonate (3a) in 71% yield. Other results are summarised in the Table.

Extension of the above method to other polyfluorinated alkyl halides is continuing. Mechanistic studies of the formation of the CF-P linkage are also in progress.

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† The proton-decoupled ³¹P n.m.r. spectrum (in CDCl₃ with H₃PO₄ capillary) consisted of a triplet of triplets of triplets at -144.5 p.p.m., *J*_{P,F} 81.1, 26.9, and 15.2 Hz.

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² D. J. Burton and R. M. Flynn, *J. Fluorine Chem.*, 1977, **10**, 329.

³ D. J. Burton and R. M. Flynn, *Synthesis*, 1979, 615.

⁴ F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565; H. J. Emeléus and J. S. Smith, *J. Chem. Soc.*, 1959, 375.

⁵ H. Brecht, *Ger. P.* 2,110,769 (1972).