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 reaction[1] 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. CF_2Br_2 (thermally)[2] and CF_3I (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 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

$$\underset{(\mathbf{1})}{R_fI} \xrightarrow{\text{i}} \underset{(\mathbf{2})}{[R_fP(OEt)_2]} \xrightarrow{\text{ii}} \underset{(\mathbf{3})}{R_fP(:O)(OEt)_2}$$

SCHEME. *Reagents:* i, $[(EtO)_2P]_2O$, Bu^tOOBu^t and $CF_2ClCFCl_2$; ii, Bu^tOOH and $MeOH–CF_2ClCFCl_2$.

TABLE. Preparation of diethyl perfluoroalkylphosphonates (**3**).[a]

Phosphonate	R_f	B.p./°C (*p*/mmHg)	Yield[b]/%
(**3a**)	n-C_6F_{13}	58—60 (1·5)	71
(**3b**)	n-C_4F_9	52—53 (7)	65
(**3c**)	iso-C_3F_7	70—72 (21)	40

[a] The ^1H, ^{13}C, ^{19}F, and ^{31}P 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 ^{19}F and ^{31}P 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 ^{31}P n.m.r. spectrum (in $CDCl_3$ with H_3PO_4 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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