

Novel Synthesis of Perfluoroalkylated α,β -Unsaturated Bromoalkane-carboxylates and -carbonitriles

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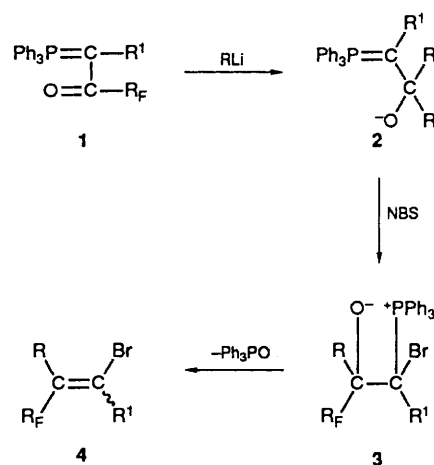
A novel synthesis of perfluoroalkylated α,β -unsaturated bromoalkane-carboxylates and -carbonitriles by the reaction of fluorinated β -oxido phosphonium ylides resulting from nucleophilic addition to β -perfluoroacyl group of fluorinated phosphoranes with *N*-bromosuccinimide is described.

Methods for the synthesis of halogenoalkenes and their fluoro species have attracted much interest, particularly in the synthesis of biologically active compounds, since they can serve as useful intermediates and undergo a variety of synthetically useful transformations.¹ However, the methods for their preparation remain limited. Although β -oxido phosphonium ylides, generated from the corresponding phosphonium ylides, aldehydes and phenyllithium, with halogenating reagents, provide a convenient route to halogenoalkenes, as first reported by Schlosser and Christmann the crude yield of bromoalkene is low (23%).² Corey *et al.* confirmed this result for the reaction with a variety of brominating agents.³ Here we report that the fluorinated β -oxido phosphonium ylides resulting from nucleophilic addition to the β -perfluoroacyl group of fluorinated phosphoranes reacts with *N*-bromosuccinimide to afford perfluoroalkylated bromoalkenes in 65–90% yields.

The organolithium compounds regioselectively attack the perfluoroacyl group of fluorinated phosphoranes **1** to give the β -oxido phosphonium ylides **2**, which react with *N*-bromosuccinimide to produce the bromo substituted betaines **3**; these spontaneously decompose to the perfluoroalkylated α,β -unsaturated bromoalkane-carboxylates and -carbonitriles **4** together with triphenylphosphine oxide.

Experimental

General Procedure.—Lithium reagent (4 mmol) was added dropwise with stirring to a solution of **1** (4 mmol) in dry THF (16 cm³) at -70°C under nitrogen. The reaction mixture was stirred for 1 h at -70°C to form **2**, which was allowed to warm to -20°C when *N*-bromosuccinimide (5 mmol) was added. After being stirred at 0°C for 1 h and 20°C for 1 h, the reaction mixture was filtered and the residue was washed with diethyl ether (20 cm³). Evaporation of the solvent gave a residue which was separated by column chromatography on silica gel



eluting with light petroleum (b.p. $60\text{--}90^\circ\text{C}$)–ethyl acetate (98:2) to give the product **4** (see Table 1). All products are new and have been characterized on the basis of microanalysis, IR, NMR spectroscopy and mass spectrometry, the details of which are available as a Supplementary publication (SUP No. 56855, 3 pp.).†

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† For details of the Supplementary publications scheme, see 'Instructions for Authors' (1992), *J. Chem. Soc., Perkin Trans 1*, 1992, Issue 1.

Table 1 Preparation of perfluoroalkylated bromoalkenes **4**

Compound	R	R _F	R'	Yield (%) ^a	Z:E ^b
4a	Ph	CF ₃	CN	90	56:44
4b	Ph	C ₃ F ₇	CN	85	60:40
4c	Bu	C ₃ F ₇	CN	66	63:37
4d	Ph	CF ₃	CO ₂ Et	85	71:29
4e	Ph	CF ₃	CO ₂ Me	83	71:29
4f	Bu	C ₃ F ₇	CO ₂ Me	65	67:33
4g	2-Thienyl	CF ₃	CO ₂ Me	84	67:33

^a Isolated yields. ^b The ratios of Z- and E-isomers were estimated on the basis of NMR spectrometry.

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