A New One-pot Synthesis of Fluorinated Bromoallenes

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A new convenient one-pot synthesis of fluorinated bromoallenes starting from the commercial available substances is described.

Halogenoallenes are potentially useful intermediates in organic synthesis, being both essential components in the synthesis of natural products such as leukotrienes ¹ and allenediynes, ² and capable of undergoing many useful transformations. Although a variety of methods have been described for the preparation of allenes, ³ it is still difficult to prepare the substituted compounds. ⁴ To the best of our knowledge, fluorinated bromoallenes have not been reported previously, although they would be expected to be useful intermediates for the preparation of fluorinated biologically active compounds. Here we report a conveient one-pot synthesis of polyfluorophenyl(bromo)allenes, starting from commercial available substances, in 62–87% yields.

The reaction sequence is as follows:

$$Ph_3 \stackrel{+}{P} - CH_2 RBr \stackrel{BuLi}{\longrightarrow} Ph_3 P = CHR \stackrel{C_6F_6}{\longrightarrow} Ph_3 P = CRC_6F_5 \stackrel{BrCH_2COBr}{\longrightarrow}$$

$$\begin{bmatrix} Ph_{3} \overset{+}{P} - C \\ Ph_{3} \overset{+}{P} - C \\ O = C - CH_{2}Br \end{bmatrix} Br \overset{-}{\longrightarrow} Ph_{3} \overset{+}{P} - C \\ O = C - \overset{-}{C}HBr \\ O = C - \overset{-}{C}HB$$

Phosphoranes 2, generated from the corresponding phosphonium salts 1 and butyllithium in tetrahydrofuran (THF), were allowed to react with hexafluorobenzene to give pentafluorophenyl(triphenyl)phosphoranes 3.5 The latter, without isolation, were then treated with bromoacetic bromide to afford the phosphonium salt 4. Deprotonation of the latter by a further molecule of 3 gave 5 which was converted into 6 via electron transfer. Triphenylphosphine oxide was then eliminated spontaneously to give the products 7.

In a typical procedure butyllithium (6 mmol in 6 ml of hexane) was added dropwise with stirring to a suspension of ethyl(triphenyl)phosphonium bromide (2.23 g, 6 mmol) in absolute THF (30 ml) at -20 °C under nitrogen. The reaction mixture was stirred for 30 min at -20 °C and

Table 1 Preparation of fluorinated bromoallenes

Compound 7	R	B.p. (°C at 2 mmHg)	Yield (%)b
a	Me	72	87
b	Et	82	81
c	Pr	86	71
d	Bu	102	84
e	Pentyl	88	62
f	Isohexyl	108	67
g	Isoheptyl ^d	110	75

^a All compounds are new and characterized by microanalyses, IR, NMR and mass spectroscopies. Detailed spectral results together with the microanalytical results are available as a Supplementary publication [SUP No. 56807, (3pp.)] † ^b Isolated yields. ^c Isohexyl = 4-methylpentyl. ^d Isoheptyl = 5-methylpexyl.

† For details of the Supplementary Publications Scheme, see 'Instructions for Authors (1991)', J. Chem. Soc., Perkin Trans. 1, 1991, Issue 1.

hexafluorobenzene (0.60 g, 3.2 mmol) was slowly added. The mixture was allowed to warm to 20 °C, stirred for 1 h, recooled to -60 °C and bromoacetic bromide (0.30 g, 1.5 mmol) was slowly added. After this addition, the mixture was stirred at 20 °C for 3 h. The product **7a** was isolated by column chromatography on silica gel (0.39 g, 87%). The results are shown in Table 1.

Acknowledgements

The authors thank the National Natural Science Foundation of China and Academia Sinica for financial support.

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Paper 0/04915H Received 18th November 1990 Accepted 28th November 1990