PHOSPHINE AND PHOSPHITE MEDIATED DIFLUOROCARBENE EXCHANGE REACTIONS OF BROM-F-METHYL PHOSPHONIUM SALTS

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Bromo- \underline{F} -methyl phosphonium salts undergo facile exchange of the bromo- \underline{F} -methyl group when treated with tertiary phosphines or trialkyl phosphites.

The mechanism of this exchange process, the influence of R' on the ease of exchange, and comparison of this salt system to other halomethyl phosphonium salts will be discussed.

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THE SYNTHESIS, METALLATION AND SYNTHETIC UTILITY OF DIALKYL-BROMO-F-METHYL PHOSPHONATES

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The title phosphonates are readily prepared in excellent yield <u>via</u> the Michaelis-Arbuzov reaction of trialkylphosphites and dibromo-F-methane. These bromo-F-methyl phosphonates are metallated directly with either cadmium or zinc powder in various solvents to give high yields of stable organometallics.

$$(RO)_3P + CF_2Br_2 \longrightarrow (RO)_2P(0)CF_2Br \xrightarrow{M} (RO)_2P(0)CF_2MX$$
 M = Cd or Zn

These metallated intermediates serve as a synthetically useful source for the introduction of the difluoromethyl phosphonate group into organic molecules. Wittig olefination gives \underline{F} -methylene olefins and acylation produces \underline{B} -ketophosphonates, which are readily cleaved with fluoride ion and serve as a convenient entry to fluoro enolates.

$$(RO)_2 P(0) CF_2 ZnX + (CF_3 CO)_2 0 \longrightarrow (RO)_2 P(0) CF_2 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = C - CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = CF_3] + (RO)_2 P(0) F_3 COCF_3 \xrightarrow{F} [CF_2 = CF_3] + (RO)_2 F_3 COCF_3 COCF_3 \xrightarrow{F} [CF_2 = CF_3] + (RO)_2 F_3 COCF_3 CO$$

The preparation of the titled phosphonates and their synthetic utility will be presented.