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THE SYNTHESIS, METALLATION AND FUNCTIONALIZATION OF BROMO-*F*-METHYL DIPHENYLPHOSPHINE OXIDE

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Bromo-F-methyl diphenylphosphine oxide is conveniently prepared via reaction of bromo-F-methane and ethyl diphenylphosphinite. Metallation with zinc provides a stable organozinc derivative in high yield.

$$Ph_2POC_2H_5 + CF_2Br_2 \longrightarrow Ph_2P(O)CF_2Br \xrightarrow{Zn} Ph_2P(O)CF_2ZnBr$$

This organozinc compound provides a useful synthetic intermediate for the introduction of the F-methylene diphenylphosphine oxide group into organic compounds. Reaction with trivalent phosphorus derivatives gives the mixed P(V)-P(III) compounds; further oxidation

$$Ph_2P(O)CF_2ZnBr + PXYZ \longrightarrow Ph_2P(O)CF_2PXY \xrightarrow{[O]} Ph_2P(O)CF_2P(O)XY$$

$X = Y = Cl, OC_2H_5, Ph$

$Z = Cl, OC_2H_5$

gives the P(V)-P(V) derivatives. The synthesis and functionalization of this new organozinc compound will be discussed.

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A NOVEL SYNTHESIS OF *gem*-DIFLUOROOLEFINS USING DIFLUOROMETHYL ENOL PHOSPHATES AND ORGANOCOPPER REAGENTS

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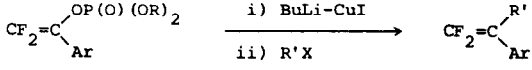
gem-Difluoroolefins have proved to be valuable intermediates in organic syntheses. In general, the difluoromethylenation of aldehydes or ketones by use of various types of difluoromethylides has been employed for preparing these compounds. We would like to report a novel synthesis of gem-difluoroolefins from difluoromethylene enol phosphates, which can easily be prepared by the reaction of chlorodifluoromethyl aryl ketones with diphenyl phosphite. The reactions of the enol phosphates with BuLi (8.2 equiv.) and CuI (5.2 equiv.) in THF containing tetramethylethylenediamine (4.0 equiv.) at -60°C, followed by treating the products with electrophiles, gave the corresponding gem-difluoroolefins in yields of 17-89%.



R = Ph; R'X = H_2O, D_2O, allyl halides

It has been found that whereas the reaction of the enol phosphates (R=Ph) proceeds as shown above, the enol phosphates (R=Et) undergo a different reaction, i.e., addition-elimination reaction, to produce butylated enol phosphates.