

## Phosphorus, Sulfur, and Silicon and the Related Elements

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## SYNTHESIS OF 1,1-DIFLUOROOLEFINS VIA WITTIG-HORNER-EMMONS REACTION

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In the presence of a catalytic amount of cuprous bromide CuBr and cosolvent acetonitrile acylation of [(diethoxyphosphinyl)difluoromethyl]zinc bromide (EtO)<sub>2</sub>P(O)CF<sub>2</sub>ZnBr, which was prepared from diethyl(bromodifluoromethyl)phosphonate (EtO)<sub>2</sub>P(O)CF<sub>2</sub>Br and zinc powder with an appropriate acylating reagents such as acetyl chloride  $CH_3C(O)Cl$ , ethyl oxalyl chloride  $ClC(O)CO_2Et$ , methyl oxalyl chloride  $ClC(O)CO_2CH_3$ , diethylcarbamoyl chloride  $ClC(O)NEt_2$ , or ethyl chloroformate ClC(O)OEt in the solvent of monoglyme or triglyme gives diethyl 2-oxo-1,1-difluoropropylphosphonate (EtO)<sub>2</sub>- $P(O)CF_2C(O)CH_3$ , ethyl difluoro(diethoxyphosphinyl)pyruvate (EtO)<sub>2</sub>- $P(O)CF_2C(O)CO_2Et$ , methyl difluoro(diethoxyphosphinyl)pyruvate  $(EtO)_2P(O)CF_2C(O)CO_2Me$ , N,N-diethyl difluoro(diethoxyphosphinyl) acetamide  $(EtO)_2P(O)CF_2C(O)NEt_2$  and ethyl (diethoxyphosphinyl) difluoroacetate (EtO)<sub>2</sub>P(O)CF<sub>2</sub>C(O)OEt occurs in good yields, respectively. However, in the preparation of  $(EtO)_2P(O)CF_2C(O)CO_2Et$ , if the acylation reaction was carried out at room temperature for 24 h in the presence of 1.5% of cuprous bromide and without using acetonitrile as cosolvent, an analogous nerve agent diethyl fluorophosphonate (EtO)<sub>2</sub>P(O)F and (EtO)<sub>2</sub>P(O)CF=CFP(O)(OEt)<sub>2</sub> were observed. Treatment of a THF solution of diethyl 2-oxo-1,1-difluorophosphonate derivatives (EtO)<sub>2</sub>P(O)CF<sub>2</sub>C(O)R (R=CH<sub>3</sub>, CO<sub>2</sub>Et, CO<sub>2</sub>Me, NEt<sub>2</sub>, OEt) with Grignard reagents R'MgX via a Wittig-Horner-Emmons reaction produces 1,1-diffuoroolefins  $R'(CH_3)C=CF_2$ ,  $R'(CO_2Et)C=CF_2$  and  $R'(NEt_2)C=CF_2.$ 

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