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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 $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{ZnBr}$, which was prepared from diethyl(bromodifluoromethyl)phosphonate $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{Br}$ and zinc powder with an appropriate acylating reagents such as acetyl chloride $\text{CH}_3\text{C}(\text{O})\text{Cl}$, ethyl oxalyl chloride $\text{ClC}(\text{O})\text{CO}_2\text{Et}$, methyl oxalyl chloride $\text{ClC}(\text{O})\text{CO}_2\text{CH}_3$, diethylcarbamoyl chloride $\text{ClC}(\text{O})\text{N}(\text{Et})_2$, or ethyl chloroformate $\text{ClC}(\text{O})\text{OEt}$ in the solvent of monoglyme or triglyme gives diethyl 2-oxo-1,1-difluoropropylphosphonate $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{C}(\text{O})\text{CH}_3$, ethyl difluoro(diethoxyphosphinyl)pyruvate $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{C}(\text{O})\text{CO}_2\text{Et}$, methyl difluoro(diethoxyphosphinyl)pyruvate $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{C}(\text{O})\text{CO}_2\text{Me}$, *N,N*-diethyl difluoro(diethoxyphosphinyl)acetamide $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{C}(\text{O})\text{N}(\text{Et})_2$ and ethyl (diethoxyphosphinyl) difluoroacetate $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{C}(\text{O})\text{OEt}$ occurs in good yields, respectively. However, in the preparation of $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{C}(\text{O})\text{CO}_2\text{Et}$, 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 $(\text{EtO})_2\text{P}(\text{O})\text{F}$ and $(\text{EtO})_2\text{P}(\text{O})\text{CF}=\text{CFP}(\text{O})(\text{OEt})_2$ were observed. Treatment of a THF solution of diethyl 2-oxo-1,1-difluorophosphonate derivatives $(\text{EtO})_2\text{P}(\text{O})\text{CF}_2\text{C}(\text{O})\text{R}$ ($\text{R}=\text{CH}_3$, CO_2Et , CO_2Me , $\text{N}(\text{Et})_2$, OEt) with Grignard reagents $\text{R}'\text{MgX}$ via a Wittig-Horner-Emmons reaction produces 1,1-difluoroolefins $\text{R}'(\text{CH}_3)\text{C}=\text{CF}_2$, $\text{R}'(\text{CO}_2\text{Et})\text{C}=\text{CF}_2$ and $\text{R}'(\text{N}(\text{Et})_2)\text{C}=\text{CF}_2$.

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