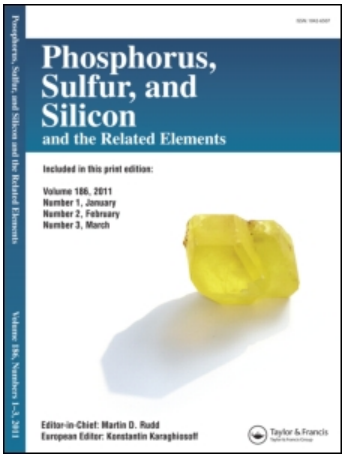

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Formation and Stability of Difluoromethylene Phospho-Raiies, $R_3P{=}CF_2$

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FORMATION AND STABILITY OF DIFLUOROMETHYLENE PHOSPHORANES, $R_3P{=}CF_2$

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Carbonyl compounds react with CBr_2F_2 in the presence of phosphanes, R_3P (R = Ph, NR'_2), and metals (M = Zn, Cd, Pb) forming geminal difluoroolefins (eq. 1)[1].

$$R'CHO + CBr_2F_2 + R_3P + M \longrightarrow R'CH{=}CF_2 + MBr_2 + R_3PO \quad (1)$$

Without any doubt this reaction has to occur via the intermediate formation of difluoromethylene phosphoranes, which then undergo the Wittig reaction with carbonyl compounds (eq. 2).

$$R_3P{=}CF_2 + R'CHO \longrightarrow R_3PO + R'CH{=}CF_2 \quad (2)$$

Up to now, however, it has not been clear, whether the difluoromethylene phosphoranes are formed via phosphonium salts like $[R_3P\text{-}CBrF_2]Br$ and their reduction (eq. 3) or by tne addition of primarily formed difluorocarbene, CF_2, to phosphanes (eq. 4).

$$CBr_2F_2 \xrightarrow{+R_3P} [R_3P\text{-}CBrF_2]Br \xrightarrow[-MBr_2]{+M} R_3P{=}CF_2 \quad (3)$$

$$CBr_2F_2 \xrightarrow[-MBr_2]{+M} CF_2 \xrightarrow{+R_3P} R_3P{=}CF_2 \quad (4)$$

Resulting from extensive experimental investigations the approach via difluorocarbene can certainly be excluded. In contrast to other methylene phosphoranes difluoromethylene phosphoranes are not stable. They will decompose into CF_2 and phosphane, if suitable reactants are absent. Ab initio MO calculations by Dixon and Smart[2] support these results.

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