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Formation and Stability of Difluoromethylene Phospho-Raies, $R_3P=CF_2$

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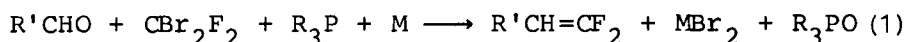
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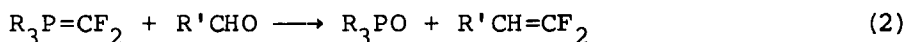
FORMATION AND STABILITY OF DIFLUOROMETHYLENE PHOSPHORANES, $R_3P=CF_2$

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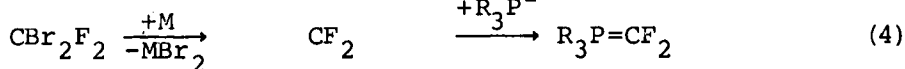
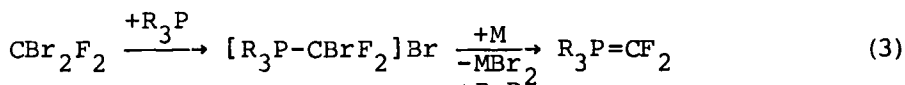
Carbonyl compounds react with CBr_2F_2 in the presence of phosphanes, R_3P ($R = Ph, NR'_2$), and metals ($M = Zn, Cd, Pb$) forming geminal difluoroolefins (eq. 1)¹.



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).



Up to now, however, it has not been clear, whether the difluoromethylene phosphoranes are formed via phosphonium salts like $[R_3P-CBrF_2]Br$ and their reduction (eq. 3) or by the addition of primarily formed difluorocarbene, CF_2 , to phosphanes (eq. 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 Smart² support these results.

1. S. Hayashi, T. Nakai, N. Ishikawa, D. J. Burton, D. G. Nae, H. S. Kesling, Chem. Lett. 1979, 983.
2. D. A. Dixon, B. E. Smart, J. Am. Chem. Soc. 108 (1986) 7172.