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Alkylation of Phosphorylmethylenetriphenylphosphoranes

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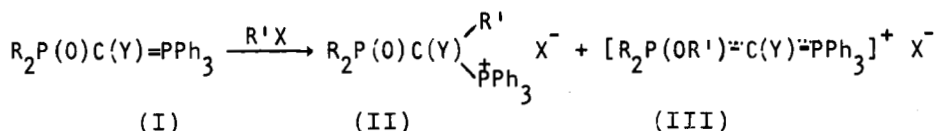
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ALKYLATION OF PHOSPHORYLMETHYLENETRIPHENYLPHOS- PHORANES

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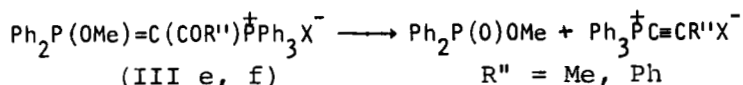
Direction of alkylation of phosphoranes (I) depends on the nature of the substituent Y and the alkylating agent. Unsubstituted phosphorane reacts with CH_3J yielding only the product of C-methylation (II), whereas the reaction with Me_2SO_4 proceeds at both ends of the OPC-triad, preferably yielding the O-alkylation product (IIIa, 80%).



Y = H (a), Ts (b), COOEt (c), P(O)Ph₂ (d), C(O)Me (e), C(O)Ph (f); R = Ph, Bu; R' = Me, Et; X = J, ClO₄, BF₄

Tosyl-, carbethoxy- and diphenylphosphoryl-substituted phosphoranes (I, b, c, d) do not react with CH_3J . Alkylation with Me_2SO_4 and $\text{Et}_3\text{O}^+\text{BF}_4^-$ proceeds at the oxygen of the PO group and stable salts (III, b, c, d) are obtained.

Methylation of acylsubstituted phosphoranes (I, e, f; R=Ph) with Me_2SO_4 proceeds at the oxygen of both PO and CO groups. The products of CO-alkylation $\text{Ph}_2\text{P}(\text{O})\text{C}(\text{P}^+\text{Ph}_3)=\text{C}(\text{OMe})\text{R}''\text{X}^-$ (IV; R'' = Me, Ph) are stable; the PO-alkylation products (III, e, f) undergo an intramolecular Wittig reaction:



Alkylation of the benzoyl substituted compound (I f) with $\text{EtO}^+\text{BF}_4^-$ yields more than 90% of the CO-ethylated product (IV, R'' = Ph). A possible explanation of the different directions of alkylation is proposed.