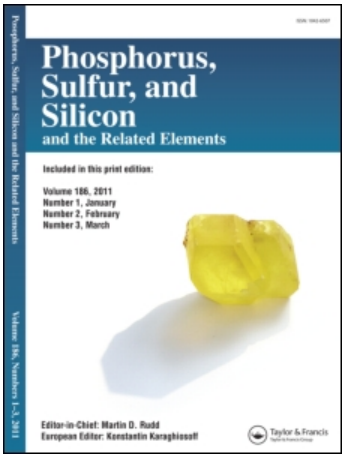

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Alkylation of Phosphorylmethylenetriphenylphosphoranes

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To cite this Article Bykhovskaya, O. V. , Aladzheva, I. M. , Leontieva, I. V. , Petrovskii, P. V. , Mastryukova, T. A. , Kabachnii, M. I. and Nesmeyanov, A. N.(1990) 'Alkylation of Phosphorylmethylenetriphenylphosphoranes', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 262

To link to this Article: DOI: 10.1080/10426509008040796

URL: http://dx.doi.org/10.1080/10426509008040796

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 262
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ALKYLATION OF PHOSPHORYLMETHYLENETRIPHENYLPHOSPHORANES

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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%).

$$R_2P(O)C(Y)=PPh_3 \xrightarrow{R'X} R_2P(O)C(Y)(R')\overset{+}{P}Ph_3\ X^- + [R_2P(OR')=C(Y)-PPh_3]^+\ X^-$$

(I) (II) (III)

Y = H (a), Ts (b), COOEt (c), $P(O)Ph_2$ (d), C(O)Me (e), C(O)Ph (f); R = Ph, Bu; R' = Me, Et; X = J, ClO_4, BF_4

Tosyl-, carbethoxy- and diphenylphosphoryl-substituted phosphoranes (I, b, c, d) do not react with CH_3J. Alkylation with Me_2SO_4 and $Et_3\overset{+}{O}BF_4^-$ 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 $Ph_2P(O)C(\overset{+}{P}Ph_3) = C(OMe)R''X^-$ (IV; R" = Me, Ph) are stable; the PO-alkylation products (III, e, f) undergo an intramolecular Wittig reaction:

$$Ph_2P(OMe)=C(COR'')\overset{+}{P}Ph_3X^- \longrightarrow Ph_2P(O)OMe + Ph_3\overset{+}{P}C{\equiv}CR''X^-$$

(III e, f) R" = Me, Ph

Alkylation of the benzoyl substituted compound (I f) with $Et\overset{+}{O}_3 \cdot BF_4^-$ yields more than 90% of the CO-ethylated product (IV, R" = Ph). A possible explanation of the different directions of alkylation is proposed.