

THE CHEMISTRY OF PHOSPHORUS AND SULFUR HALIDES. ALKYL TRANSFER
FROM BORANES.

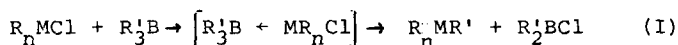
P.M. Draper, T.H. Chan¹ and David N. Harpp¹

Department of Chemistry

McGill University, Montreal, Canada.

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Consideration of the reactions of alkylboranes with chloramine² and carbon monoxide³ has led us into the investigation of the possibility of alkyl transfer from boron to phosphorus or sulfur as a potential method for the synthesis of organophosphorus and sulfur compounds. While the formation of trivalent phosphorus - boron and divalent sulfur-boron complexes are well known⁴, the reactions depicted by equation I have not, to our knowledge, been investigated.



M = S, n = 1

M = P, n = 2.

We wish to present evidence to demonstrate that it is possible to alkylate chlorophosphines and sulfenylchlorides and that these reactions may constitute a viable synthesis of organophosphorus and organosulfur compounds.

When diphenylchlorophosphine was refluxed with a molar equivalent of tricyclohexylborane in tetrahydrofuran for two hours, a 48% yield of cyclohexyldiphenylphosphine oxide was obtained. Since the phosphine is oxidized very rapidly during the work-up and the oxide is usually easier to handle, no attempt was made to isolate the phosphine itself. Phosphine oxides can quantitatively be reduced to phosphines by trichlorosilane^{5a} or hexachlorodisilane^{5b}. The yield of cyclohexyldiphenylphosphine oxide could be increased to 57% by refluxing the reaction mixture in a higher boiling solvent, e.g. di-n-butyl ether. The use of excess trialkylborane or longer reaction time did not significantly

improve the yield. The reaction of diphenylchlorophosphine with tri-n-octyl borane gave the expected n-octyl-diphenylphosphine oxide in better than 50% yield.

The reaction of sulfenylchlorides with alkylboranes was also investigated. When p-toluenesulfenylchloride was heated with a molar equivalent of tri-n-octylborane in di-n-butyl ether, p-tolyl-n-octylsulfide was formed in 37% yield (vpc). Similarly, benzenesulfenyl chloride gave phenyl-n-octylsulfide in 20% yield (vpc).

Alkyl migration from alkylboranes to chlorophosphines and sulfenyl chlorides appears thus to be a general reaction⁶. We are investigating the application of this reaction for the synthesis of novel organophosphorus and organosulfur compounds.

References

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