Tetrahedron Letters No.20, pp. 1687-1688, 1970. Pergamon Press. Printed in Great Britain.

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

P.M. Draper, T.H. Chan[1] and David N. Harpp[1]
Department of Chemistry
McGill University, Montreal, Canada.

(Received in USA 25 February 1970; received in UK for publication 2 April 1970)

Consideration of the reactions of alkylboranes with chloramine[2] and carbon monoxide[3] 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 known[4], the reactions depicted by equation I have not, to our knowledge, been investigated.

$$R_nMCl + R'_3B \rightarrow \left[R'_3B \leftarrow MR_nCl\right] \rightarrow R_nMR' + R'_2BCl \qquad (I)$$

$$M = S,\ n = 1$$
$$M = P,\ n = 2.$$

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 trialkyborane 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 sufenylchlorides 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 reaction[6]. We are investigating the application of this reaction for the synthesis of novel organophosphorus and organosulfur compounds.

References

(1) To whom enquiries can be addressed.

(2) H.C. Brown, W.R. Heydkemp, E. Breuer and W.S. Murphy, J.Am. Chem. Soc., 86, 3565 (1964).

(3) H.C. Brown, Accounts Chem. Research. 2, 65 (1969).

(4) (a) G.M. Phillips, J.S. Hunter and L.E. Sutton, J. Chem. Soc., 146 (1945); (b) M.F. Lappert, J. Chem. Soc., 2781 (1953); (c) K.C. Nainan and G.E. Ryschkewitsch, Inorg. Chem., 8, 2671 (1969) and references cited therein.

(5) (a) H. Fritzsche, U. Hasserodt and F. Korte, Chem. Ber., 98, 171 (1965); (b) K. Naumann, G. Zon and K. Mislow, J. Am. Chem. Soc., 91, 7012 (1969).

(6) In a patent, alkyl migration from aluminum to phosphorus was claimed R.E. Hall, A. Kessler and A.R. McLain, U.S. Patent 3, 459, 808; Chem. Abst., 71, 81524 (1969); O. Yu, O. Khlobystin and L.I. Zakharkin, Izvest. Akad. Nauk. S.S.S.R., Otedel. Khim. Nauk 1006, (1958) Chem. Abst., 53, 1122 (1959).

Acknowledgement: Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for financial support of this research.