Sulphur Atom Transfer in Diphenylthiophosphoryl(diorganophosphino)methanes

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Summary Sulphur atom transfer between phosphorus atoms occurs readily upon heating diphenylthiophosphoryl(dimethylphosphino)methane and produces dimethylthiophosphoryl(diphenylphosphino)methane.

The sulphur exchange reactions of tri-n-butylphosphine with sulphides of tertiary phosphines of lesser basicity are well known.[1] However, we have observed a unique reaction in which sulphur atom transfer occurs between phosphorus atoms in the same molecule. The product is obtained in good yield, and the reaction provides additional examples of the relatively new class of compound,[2,3] phosphine-phosphine sulphides, which contain tervalent and quinquevalent phosphorus atoms in the same molecule. Thus, heating $Ph_2P(S)CH_2PMe_2$ in diethylene glycol dimethyl ether (160° for 30 h) gave $Ph_2PCH_2P(S)Me_2$ (conversion 85%, isolated 50%), in which the sulphur atom has moved from the less basic phosphorus atom to the more basic phosphorus atom. The reaction has also been carried out in good yield (>60%) for $Ph_2P(S)CHR^1R^2$ ($R^1 = Ph$, $R^2 = Me$ or Pr^i; $R^1 = R^2 = Pr^i$). The larger steric requirements of the Pr^i group do not appear to decrease the reaction rate nor lower the yield. In fact the isolated yields of the isopropyl containing compounds were *ca.* 80%.

The progress of the reaction can be followed conveniently by ^1H and/or ^{31}P n.m.r. spectroscopy. For example, with $Ph_2P(S)CH_2PMe_2$, the methyl doublet [δ, 1·08; ^2J(P–H), 3·8] of the dimethylphosphino group diminishes in intensity as the methyl doublet of doublets [δ, 1·64; ^2J(P–H), 13·2; ^4J(P–H), 0·9] of the dimethyl thiophosphoryl group grows during the course of the reaction. Preliminary kinetic experiments indicate that the reaction is neither simple first order (as would be expected from an intramolecular sulphur 'jump') nor simple second order. In addition, two intermediates, $Ph_2P(S)CH_2P(S)Me_2$ and $Ph_2PCH_2PMe_2$, have been identified as being present in roughly equal and constant amounts throughout the course of the reaction, after a brief initiation period. These intermediates compose <10% each of the total methyl signal in the n.m.r. spectrum Thus the mechanism of the reaction, which is under further study, is rather complex.

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[1] L. Maier, 'Organic Phosphorus Compounds,' vol. 1, eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, p. 47.
[2] D. Seyferth, U.S.P. 3,426,021, Feb. 1969; *Chem. Abs.*, 1969, **71**, 39167a.
[3] S. O. Grim and J. D. Mitchell, *Syn. React. Inorg. Metal-org. Chem.*, 1974, **4**, 221.