

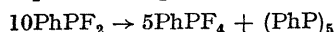
The Disproportionation of Phenyldifluorophosphine

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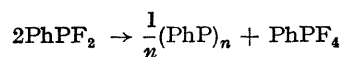
Summary Polymeric phenylphosphines are formed on spontaneous disproportionation of phenyldifluorophosphine under nitrogen at room temperature.

ANG and SCHMUTZLER¹ recently reported the spontaneous disproportionation of phenyldifluorophosphine to pentaphenylpentaphospholan and phenyltetrafluorophosphorane:



While the constitution of all forms of the phenylphosphines, $(\text{PhP})_n$, is not established,^{2,3} it is agreed that at least three species exist: Form A ($n = 5$, m.p. 149–150°), Form B ($n = 6$, m.p. 190°), and at least one (presumed polymeric) form of unknown molecularity which melts within the range 252–285°, and is insoluble in organic solvents. Henderson *et al.*⁴ have distinguished two high melting forms, C and D, melting within the ranges 270–283° and 260–285°, respectively.

On the basis of observed melting point (151–154°), and comparison of the X-ray diffraction pattern with that of an authentic sample, Ang and Schmutzler¹ report that the disproportionation product is the pentamer, Form A. However, this disproportionation was observed in these laboratories some years ago,⁵ and has been re-checked recently. Both phenyldifluorophosphine, and an equimolar mixture of phenyldifluorophosphine and phenyl-dichlorophosphine, allowed to stand at room temperature under nitrogen, deposit a white powder, insoluble in organic solvents, which melts near 280°. This clearly indicates the production of a polymeric form, probably D,:



and not A, as found by Ang and Schmutzler.¹ Samples of our product re-melted at 150°, and were then soluble in organic solvents, as previously noted elsewhere⁶ for D.

An X-ray diffraction pattern for our product further confirmed that it was not Form A, but was markedly similar to the corresponding (identical) patterns⁷ obtained for authentic samples of Forms C and D, although minor differences in both intensities and line sequence were noted.

There is at present no reproducible synthetic route^{2,4} to the polymeric phenylphosphines. Although interconversion from Form A, (which is readily prepared) to Form C *via* warming in piperidine at 80° has been reported,³ we have had little success with this procedure. Hence direct formation of a polymeric form from the above disproportionation represents a simple synthesis from readily available precursors.

Identical samples of polymeric phenylphosphine were obtained from disproportionation experiments of very different time-span (2 days and some months). It is therefore difficult to reconcile the difference in product obtained in these experiments and those reported earlier.¹ However, it seems clear that the polymeric form(s) is thermally unstable with respect to the pentamer, and lack of synthetic reproducibility is apparently⁴ a feature of these systems.

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