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PHENYLTHIO- AND PHENYLSELENO-DIPHENYL PHOSPHINE

R. A. N. McLEAN

School of Chemistry, The University,
Bristol 8, United Kingdom.

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Although a number of alkylthiodiphenylphosphines (phosphinothioite alkyl esters) have been known for some time (1-5), we reported the preparation of the first arylthiodiphenylphosphine as late as 1966 (6). Further study has revealed that phenylthiodiphenylphosphine is less stable to oxidation than was at first thought, and we have been informed that difficulty has been experienced with its preparation (7).

We have investigated further the preparation of phenylthiodiphenylphosphine (Ph_2P-SPh) and its selenium analogue in detail and have observed some important differences, which can be rationalised by consideration of the relative strengths of the organo-sulphur and organo-selenium bonds. In particular, it was noticed that phenyl selenodiphenylphosphine undergoes an Arbusov rearrangement to triphenylphosphine selenide more readily than the corresponding sulphur compound, and is much more easily oxidised.

These points are illustrated in the preparative details which follow.

The reaction between diphenylchlorophosphine and sodium thiophenolate, carried out in ether solution at 0° with rigorous exclusion of oxygen produces an 80-90% yield of the required phenylthiodiphenylphosphine, m.p. 52° (Anal. Calcd. for $C_{18}H_{15}PS$: C 73.22, H 5.09, S 10.87, P 10.82. Found: C 72.74, H 5.03, S 10.91, P 10.65). However, if air is not rigorously excluded, oxidation occurs to give the phosphine oxide, $Ph_2P(O)SPh$, m.p. 90-92° (Anal. Calcd. for $C_{18}H_{15}OPS$: C 69.50, H 4.82, S 10.30. Found: C 69.49, H 4.92, S 10.28).

As the temperature is raised, an increasing proportion of the Arbusov rearrangement product, triphenylphosphine sulphide ($Ph_3P=S$), is formed, until in refluxing solvent this is the sole product.

When dry, phenylthiodiphenylphosphine is slowly oxidised in air to $Ph_2P(O)SPh$. On prolonged heating in a sealed tube at 100°, it slowly isomerises to $Ph_3P=S$.

If diphenylchlorophosphine undergoes reaction with sodium selenophenolate (NaSePh) at 0° in ether under nitrogen, the product is triphenylphosphine selenide (m.p. 185°), and even at lower temperatures this is the major product.

Phenylselenodiphenylphosphine was prepared by adding diphenylchlorophosphine to an equimolar quantity of benzeneselenol and slight excess of triethylamine in ether under nitrogen at -10°C. Recrystallisation of the crude material from chloroform hexane, and subsequent vacuum distillation (130° at 0.07 mm Hg) produced a 50% yield of the pure pale yellow product, $Ph_2P-SePh$ (m.p. 54°, mixed m.p. with Ph_2Se_2 40°. Anal: Calcd. for $C_{18}H_{15}PSe$: C 63.2, H 4.4. Found: C 63.8, H 4.1). Despite precautions to eliminate oxygen, some of the remainder of the yield was the less soluble, white phosphine oxide $Ph_2P(O)SePh$ (m.p. 95°. Calcd. for $C_{18}H_{15}OPSe$: C 60.5, H 4.2. Found: C 60.6, H 4.3).

Phenylthiodiphenylphosphine can be prepared in 90% yield by the method used for phenylselenodiphenylphosphine.

Phenylselenodiphenylphosphine is oxidised to $Ph_2P(O)SePh$ within a few hours. It isomerises to $Ph_3P=Se$ on heating at 100° for three to four hours, hence another reason for the low yield in the preparation.

The readier Arbusov rearrangement of the selenium compound can be explained by the weaker carbon-selenium bond. The easier oxidation is possibly due to the lower electronegativity of selenium producing a higher electron density on the phosphorus atom.

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