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Rearrangement of *O*-Benzoyl-*N*-(diphenylphosphinothioyl) hydroxylamine: An ^{18}O-Labelling Investigation of Oxygen-Sulfur Transposition

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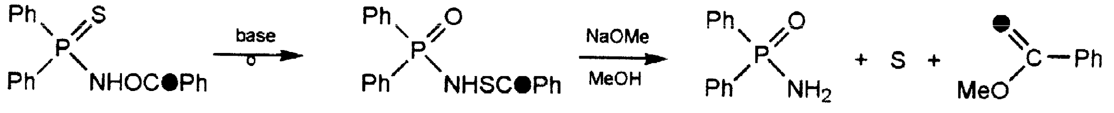
Abstract: When $Ph_2P(S)NHOCOPh$ labelled with ^{18}O in the C=O group (43% isotopic enrichment) reacts with NaOMe in MeOH, the products are unlabelled $Ph_2P(O)NH_2$ and labelled $PhCO_2Me$ (43% isotopic enrichment). By implication, the intermediate $Ph_2P(O)NHSCOPh$ that results from rearrangement (transposition of O and S atoms) has all the label in the C=O group and none in the P=O group.

N-Phosphinoylhydroxylamines [$R_2P(O)NHOH$] are the phosphorus analogues of hydroxamic acids and their chemistry has received considerable attention.[1] Much less is known about the thiophosphinoyl compounds, although $Ph_2P(S)NHOH$ has been prepared and characterised, as has its *O*-benzoyl derivative.[2] With methoxide $Ph_2P(S)NHOCOPh$ loses sulfur and forms $Ph_2P(O)NH_2$, not directly but after rearrangement to $Ph_2P(O)NHSCOPh$.[2] We have now examined this unusual rearrangement by means of ^{18}O labelling.

Labelled benzoyl chloride was obtained from the unlabelled material by hydrolysis with $H_2{}^{18}O$ (*ca.* 90 atom % ^{18}O) in pyridine and treatment of the product with oxalyl chloride (DMF catalyst). On reaction with $Ph_2P(S)NHOH$ in CH_2Cl_2 (containing Et_3N) it afforded the labelled substrate **1** (● = ^{18}O), m.p. 95.5-97.5 °C (lit.,[2] 95.5-97 °C for unlabelled material), $\delta_P(CDCl_3)$ 65.5, ν_{max}(Nujol) 3180 (NH), 1730 (C=O) and 1700 (C=^{18}O) cm^{-1}; the mass spectrum (M^+ 353 and 355) indicated an enrichment of 43% one ^{18}O atom.



Scheme 1 **1** **2** **3** **4**

With methanolic NaOMe (1.2 equiv; 0.4 mol dm^{-3} initially; 20 min) the substrate **1** was converted into the phosphinic amide **3**, δ_P 25.3; methyl benzoate **4**, ν_{max} 1725 (C=O) and 1700 (C=^{18}O) cm^{-1}; and elemental sulfur.[3] Mass spectrometry revealed negligible (<1%) ^{18}O enrichment for the phosphinic amide **3** (M^+ 217 and 219, ratio 98.8 : 1.2 *c.f.* 99.4 : 0.6 for natural abundance material) but 43 atom % enrichment for the ester **4** (M^+ 136 and 138, ratio 56.6 : 43.4), the same as in the substrate.[4] The implication is clear: the benzoyl C=O group retains its identity in the rearrangement of **1** to **2** (Scheme 1); no ^{18}O is transferred to the P=O group and none is lost from the C=O group.

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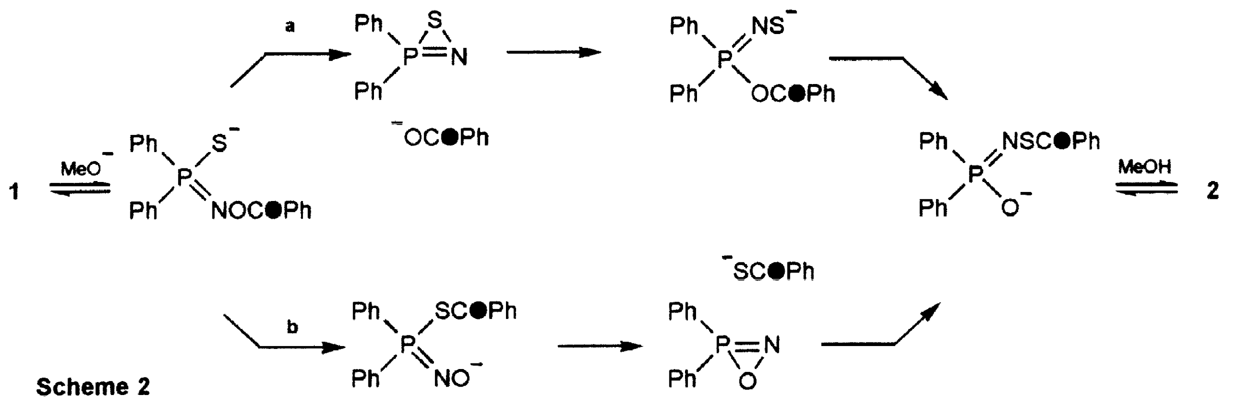
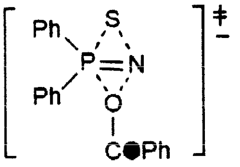
In the mechanism previously proposed (Scheme 2, path a)[2] the conjugate base of **1** first fragments, by intramolecular nucleophilic attack of sulfur: benzoate is displaced from the N atom but returns at phosphorus and benzoyl transfer to the S atom then gives the conjugate base of **2**. The benzoate anion might well return so quickly that its O atoms are only partially equilibrated, and the label only partially scrambled, but our results require that there be no equilibration at all.[5] The identity of the benzoate C=O group could be preserved by a concerted migration, but only if it proceeded by way of transition state **5**; the more plausible transition state **6** would not suffice. Perhaps the initial attack of sulfur is not, in fact, on the N atom, but on the benzoyl C=O group instead (Scheme 2, path b): the anion that is subsequently liberated by fragmentation would then be thiobenzoate, not benzoate, and there would be no question of O atom equilibration. In accord with this, the rearrangement of **1** (unlabelled) in the presence of ArCOS$^-$ (Ar = *p*-tolyl) gave $Ph_2P(O)NHSCOAr$ as well as **2**, as evidenced by the formation of $ArCO_2Me$ as well as **4**. Unfortunately, it is not possible to distinguish between the formation of $Ph_2P(O)NHSCOAr$ in the rearrangement and its formation from **2**, by rapid exchange with ArCOS$^-$, subsequent to rearrangement. Independent evidence for or against the alternative mechanism is therefore still required.



Scheme 2



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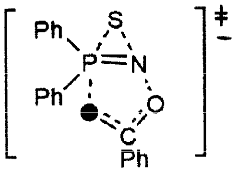

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REFERENCES AND NOTES

1. Harger, M. J. P.; Shimmin, P. A. *Tetrahedron*, 1992, **48**, 7539 and references cited therein.
2. Harger, M. J. P. *Tetrahedron Lett.*, 1993, **34**, 7947.
3. The salt $Ph_2P(S)ONa$ (δ_p 56.4; 7%) was a minor product; it showed no ^{18}O enrichment.
4. Mass spectra were recorded in EI mode (70 eV). The relative abundance of M^+ was 22% for **2**, 55% for **3** and 35% for **4**.
5. Return with partial equilibration of O atoms is often seen for ion pairs (Creary, X.; Inocencio, P.A. *J. Am. Chem. Soc.*, 1986, **108**, 5979 is especially pertinent). In Scheme 2 the anion returns to a neutral species, not a cation, and the scope for equilibration of the O atoms could be greater.