

METHOXIDE-CATALYSED REARRANGEMENT OF N- TO O-(DIPHENYLPHOSPHINYL)HYDROXYLAMINE

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Summary. In methanol $\text{Ph}_2\text{P}(\text{O})\text{NHOH}$ undergoes rapid NaOMe-catalysed rearrangement to $\text{Ph}_2\text{P}(\text{O})\text{ONH}_2$ which is subsequently converted into $\text{Ph}_2\text{P}(\text{O})\text{ONa}$ and $\text{Ph}_2\text{P}(\text{O})\text{OMe}$.

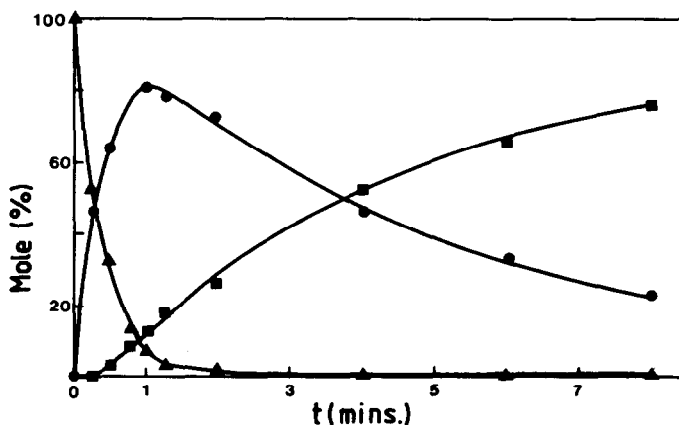
N-Phosphinylhydroxylamines such as 1 have been prepared only recently,¹ and their chemistry remains largely unexplored. As structural analogues of hydroxamic acids² they might be expected to form stable salts with alkali, but we now report that this is not the case.



N-(Diphenylphosphinyl)hydroxylamine 1 dissolves only slowly in aqueous NaOH and ³¹P n.m.r. spectroscopy shows that the solution does not contain the conjugate base of 1; rather it consists entirely of the phosphinate anion 2 resulting from hydrolysis and/or decomposition. In methanol solution 1 (0.040 M) reacts with NaOMe (1.0 equiv.) over ca. 20 min at 26 °C to give comparable amounts of the phosphinate anion 2 and ester 3. Using ³¹P n.m.r. spectroscopy it can be seen that 1 (δp 29.6) is completely consumed within 3 min (t_{1/2} ~ 0.3 min) but the products 2 (δp 19.9) and 3 (δp 34.7) form relatively slowly (Figure).³ The intermediate (δp 38.1) that is dominant in the early stages of the reaction was isolated from a reaction quenched (AcOH) after 1.3 min; on concentrating and cooling, crystals of O-(diphenylphosphinyl)hydroxylamine 4 (61%) were obtained, identical with the sample previously prepared by direct phosphinylation of H₂NOH.⁴ Separate experiments confirmed that both the rate (t_{1/2} ~ 3.5 min at 26 °C) and the products [(2) + (3), ratio ~ 1] of the reaction of 4 with NaOMe (1 equiv.) in methanol are compatible with it being the only product formed directly from 1.

FIGURE Reaction of 1 in MeOH with NaOMe (1 equiv.) at 26 °C: Composition of the mixture at different times. (Data obtained by ³¹P n.m.r. analysis of samples quenched with AcOH.)

- ▲ $\text{Ph}_2\text{P}(\text{O})\text{NHOH}$
- Intermediate
- $\text{Ph}_2\text{P}(\text{O})\text{O}^- + \text{Ph}_2\text{P}(\text{O})\text{OMe}$

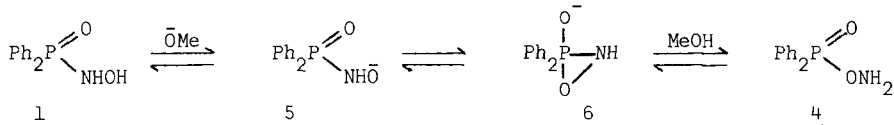


The rearrangement of 1 to 4 is reminiscent of that which occurs in the acylation of H_2NOH , although there it is the kinetically-preferred O-acylhydroxylamine that isomerises to the more stable N-acyl compound.⁵ Also, whereas H_2NOH is the specific catalyst for the rearrangement of acylhydroxylamines,⁵ it does not promote the interconversion of 1 and 4 in methanol (in the absence of alkali). Use of less than 1.0 equiv. of NaOMe shows that it acts catalytically in the rearrangement of 1 (Table), but because it is consumed in the subsequent breakdown of 4 some 0.15 equiv. is needed for complete conversion of 1.⁶

TABLE Reaction of 1 in MeOH with different amounts of NaOMe: Composition of the mixture when reaction ceases.

NaOMe (equiv.)	0.05	0.10	0.15	0.20	1.00
$\text{Ph}_2\text{P}(\text{O})\text{NHOH}$ (%)	24	8	0	0	0
$\text{Ph}_2\text{P}(\text{O})\text{ONH}_2$ (%)	67	78	71	62	0
<u>2</u> + <u>3</u> (%)	9	14	29	38	100

Mechanistically the rearrangement of 1 to 4 could be intermolecular with methoxide acting as a nucleophile, but since 3 is not converted into 4 under the conditions of the reaction this seems unlikely. An alternative would involve methoxide as a base; the anion 5 could then rearrange by intramolecular nucleophilic attack with formation of a three-membered cyclic phosphorane intermediate 6. The subsequent breakdown of 4 presumably involves competing attack of



methoxide at phosphorus to give 3 and on the NH_2 group to give 2. If this can be prevented the rearrangement of 1 may prove useful since 4 shows promise as an electrophilic aminating agent.^{7,8}

References and Footnotes

1. M.J.P. Harger, *J. Chem. Soc., Chem. Commun.*, 1979, 930.
2. H.L. Yale, *Chem. Rev.*, 1943, 33, 209; L. Bauer and O. Exner, *Angew. Chem. Int. Edn. Engl.*, 1974, 13, 376.
3. The ratio 2/3 was >1 in the early stages but tended towards 1 as reaction proceeded.
4. M.J.P. Harger, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3284.
5. W.P. Jencks, *J. Am. Chem. Soc.*, 1958, 80, 4581, 4585; T.C. Bruice and L.R. Fedor, *J. Am. Chem. Soc.*, 1964, 86, 739.
6. For both 1 and 4 the product ratio 2/3 was ~ 1 using 1 equiv. NaOMe but ~ 2 with 0.1-0.2 equiv. and ~ 0.5 with 10 equiv.
7. e.g. E.W. Colvin, G.W. Kirby, and A.C. Wilson, *Tetrahedron Lett.*, 1982, 3835.
8. Compounds related to 4 have been postulated as unstable intermediates in the phosphorylation of H_2NOH , e.g. B.J. Jandorf, *J. Am. Chem. Soc.*, 1956, 78, 3686.

(Received in UK 16 May 1983)