Conversion of Phosphinic into Phosphinous Esters through Nickelocene Reduction–complexation of Phosphinothioic *O*-Esters. A New Synthesis of Carbon–phosphorus Heterocycles

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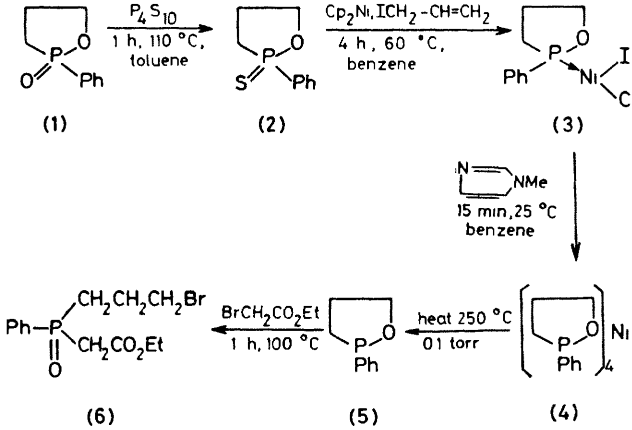
Summary A new procedure for reducing a phosphinate (LO) into the corresponding phosphinite (L) includes the following steps: LO → LS → CpNi(I)L → NiL_4 → L (Cp = cyclopentadiene); such a scheme is illustrated by the syntheses of 2-phenyl-1,2-oxaphospholane and 2-phenylisophosphindoline 2-oxide.

At present there is no general, well established procedure for reducing a phosphinate $R^1_2P(O)OR^2$ into the corresponding phosphinite $R^1_2POR^2$.[1] Classical reduction methods cannot discriminate between the P–O single and double bonds of a phosphinate.[2] Our goal was thus to devise such a method by taking advantage of two previously established facts: both the P=O → P=S conversion by P_4S_{10}[3] and the nickelocene reduction–complexation of P=S groups[4] can be applied to the P–O(C) bond of a phosphinate. We tested this with the 1,2-oxaphospholane system (Scheme 1).

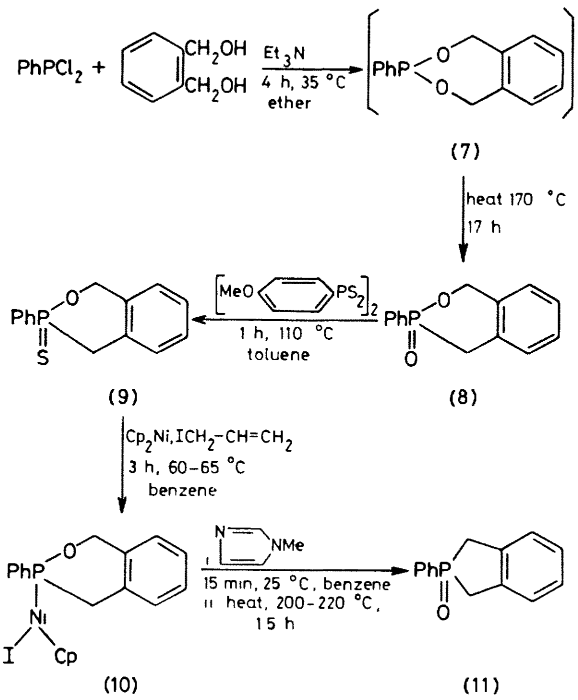


Scheme 1

The first two steps are detailed in reference 4. In the third step complex (**3**) (1·3 g) was vigorously stirred under argon with *N*-methylimidazole (1·4 ml) in deoxygenated benzene (10 ml). The solution turns green, then violet. The volatile products were pumped off under vacuum (0·1 torr, 60 °C, 1 h) and complex (**4**) extracted from the residue with hexane (yield 55%). Complex (**4**) is a yellow crystalline (MeOH) solid, very sensitive toward oxygen, which was mainly characterized by mass and n.m.r. spectroscopy: *m/e* (70 eV) 722 and 724 (*M*, 1%); 556 and 558 (*M* −L, 2%); 390 and 392 (*M* −2L, 3%); 224 and 226 (*M* −3L), 1%); and 166 (L, 100%) [L = (**5**)]; δ (^{31}P) (C_6D_6; 85% H_3PO_4 as external standard, downfield shifts + ve) 129 p.p.m.; δ (^1H) (C_6D_6; Me_4Si as internal standard) 1·33 (m, 2H C-CH_2-C); 1·97 (d.m., 2H, P–CH_2); 3·80 (m, 2H, O–CH_2); and 7·0—7·4 (m, 5H, Ph).

The final step is a kugelrohr distillation which gives (**5**) as a readily oxidizable liquid [b.p. *ca.* 100 °C/0·1 torr] in 65% yield. This product was characterized by ^1H and ^{31}P n.m.r. spectroscopy in comparison with the literature data[5]: δ (^{31}P) (C_6D_6) 107·5 p.p.m. It was further identified by its Arbuzov reaction with ethyl bromacetate which gives the expected product (**6**) in 57% yield. The reaction was performed without solvent and (**6**) was purified by chromatography on silica gel (AcOEt–MeOH 90:10): δ (^1H) ($CDCl_3$) 1·12 (t, 3H, O–CH_2–CH_3); 2·21 (m, 4H, P–CH_2–CH_2); 3·10 [d, ^2J (H–P) 14 Hz, 2H, P–CH_2–CO_2Et]; 3·39 (t, 2H, CH_2Br); 3·95 (q, 2H, O–CH_2–CH_3); and 7·43 (m, 5H, Ph); δ (^{31}P) ($CDCl_3$) 32·1 p.p.m.; i.r.: ν(CO) 1720 cm^{-1} ($CDCl_3$): mass spectrum (70 eV): *m/e* 334 and 332 (*M*, 21%); 253 (*M* −Br, 100%).

The most noteworthy feature of this sequence is undoubtedly the original conversion of complex (**3**) into complex (**4**), the mechanism of which is not understood as yet. Since NiL_4 complexes (L = P donor) are catalytically useful, this adds a new dimension to such a result. However, the main interest in a method for reducing phosphinates to phosphinites lies in the possibility of building two successive P–C bonds by Arbuzov reactions when starting with a phosphonite. Thus, it becomes possible to devise a new route toward carbon–phosphorus heterocycles which is illustrated by a new synthesis of the isophosphindoline ring (Scheme 2). Phosphonite (**7**) can be distilled (130 °C, 0·1 torr) and has been characterized by n.m.r. spectroscopy: δ (^{31}P) (C_6D_6) 111·7 p.p.m.; δ ^1H ($CDCl_3$) 4·95 (m, 4H, CH_2–O) and 6·97—7·15—7·50 (m, 9H, Ph). However, it is usually directly pyrolysed at atmospheric pressure under argon to give in 60% overall yield, the phosphinate (**8**), which is also purified by distillation (210 °C, 0·1 torr) [m.p. 120 °C (C_6H_6); δ ^{31}P ($CDCl_3$) 31·1 p.p.m.; δ ^1H ($CDCl_3$) 3·25 [d, ^2J(H–P) 14·5 Hz, 2H, CH_2–P]; 4·66—5·57 (m, 2H, CH_2–O); and 7·05—7·40 (m, 9H, Ph)]. For the P=O → P=S conversion we have used a smoother reagent than P_4S_{10} which has been previously introduced by Pedersen *et al.* for the C=O → C=S conversion.[6] Phosphino-thioate (**9**) was purified by chromatography on silica gel (hexane–C_6H_6 20:80), yield 75%. [m.p. 77 °C (hexane–CCl_4 80:20); δ (^{31}P) ($CDCl_3$) 77·1 p.p.m.; δ (^1H) ($CDCl_3$) 3·41 (m, 2H, CH_2–P); 4·63—5·53 (m, 2H, CH_2–O); and 7·0—7·7 (m, 9H, Ph)]. The reduction–complexation was performed by heating a mixture of (**9**) (2·6 g), Cp_2Ni (5·7 g), and allyl iodide (1 ml) in benzene (50 ml). The red complex (**10**) was chromatographed on silica gel (C_6H_6), yield 3·8 g (75%) [m.p. 133 °C (EtOH–C_6H_6 80:20); δ (^{31}P) (C_6D_6) 131·9 p.p.m.; δ (^1H) (C_6D_6) 3·4—4·0 (m, 2H, CH_2–P); 4·4 (m, 2H, CH_2–O); 5·10 (s, 5H, Cp); 6·8 (m, 7H, Ph); and 7·6 (m, 2H, PhP: H *ortho*); mass spectrum (70 eV) *m/e* 478 and 480 (*M*, 27%); 351 and 353 (*M* —I, 13%); 250 and 252 (*M* —L, 23%); and 228 (L, 100%)]. Complex (**10**) was allowed to react with *N*-methylimidazole in the same way as complex (**3**). The ether extracts of the reaction residue were directly pyrolysed under 0·1 torr. The phosphindoline oxide (**11**) was distilled, yield 38% (not optimized) [m.p. 99 °C (cyclohexane, with $1H_2O$); δ (^{31}P) ($CDCl_3$) 52·4 p.p.m.; δ (^1H) ($CDCl_3$) 3·27—3·44—3·51 (ABX system, 4H, CH_2–P) and 7·15—7·50 (m, 9H, Ph); mass spectrum (70 eV) *m/e* 228 (*M*, 100%); 104 [*M* —(PhP=O), 52%]. These data are in agreement with the literature[7]].



SCHEME 2

This route may well lead to carbon–phosphorus heterocycles of various sizes and with various functional substitutions (the reduction–complexation step does not interfere with the main organic groups[8]).

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[1] It is possible to convert an ethyl phosphinate into the corresponding ethyl phosphinite by reduction with Mg after *O*-alkylation of the phosphoryl group with $Et_3O^+BF_4^-$: A. Rhomberg and P. Tavs, *Monatsh. Chem.*, 1967, **98**, 105. Of course this method is valid only for ethyl esters.

[2] It is well known that $LiAlH_4$ reduces first the P–O(C) bond of phosphinates: T. L. Emmick and R. L. Letsinger, *J. Amer. Chem. Soc.*, 1968, **90**, 3459, and that silanes cannot discriminate between P=O and P–O(C) bonds and yield directly secondary phosphines: H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, 1965, **98**, 1681.

[3] See for example: J. Omelańczuk and M. Mikolajczyk, *Tetrahedron*, 1971, **27**, 5587 and reference cited herein.

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[6] B. S. Pedersen, S. Scheibye, N. H. Nilsson, and S. O. Lawesson, *Bull. Soc. chim. belges*, 1978, **87**, 223.

[7] E. D. Middlemas and L. D. Quin, *J. Org. Chem.*, 1979, **44**, 2587 and references cited herein.

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