The Reaction of the Diarylphosphine Oxide Anion with Oxiranes: a New Synthesis of 1,2-Ethylenebis(diarylphosphine oxides)

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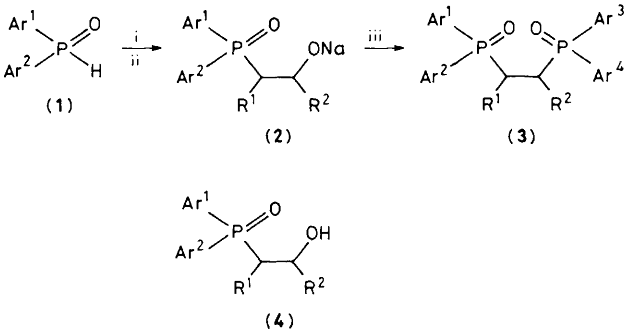
In an unusual double-substitution reaction, the diarylphosphine oxide anion reacts with oxiranes to give bis(phosphine oxides) that can have functional groups on the aryl ring and/or the bridging carbons between the PO groups.

We have recently reported that the secondary phosphine oxide anion can be used to considerable advantage, as a soft nucleophile, in a high-yield preparative method for a series of substituted 1,2-ethylenebis(diarylphosphine oxides).[1] Upon



Scheme 1. i, NaH–DMF; ii, $R^1CH–O–CHR^2$, 70 °C; iii, $Ar^3Ar^4P(O)Na$–DMF. Ar = C_6H_5, C_6H_4OMe-*o*, C_6H_4OMe-*p*; R^1 = H; R^2 = H, Me, C_6H_5, C_6H_4OMe-*p*; and R^1,R^2 = $-[CH_2]_4-$.

reduction, bis(phosphines) are formed which are useful as bidentate ligands in transition metal catalysed reactions in order to investigate the influence of the substituent groups on the environment close to the chelated metal centre.[2] We now describe how the powerfully nucleophilic diarylphosphine oxide anion can also be treated with the oxirane moiety to afford, in high yield, bis(phosphine oxides) (**3**), which we obtained previously[1] from 1,2-bis(toluene-*p*-sulphonates), in an unusual double-substitution reaction.

The anion is generated in *N,N*-dimethylformamide (DMF) from the diarylphosphine oxide (**1**) by reaction with sodium hydride (1 equiv.), which gives a characteristically yellow homogeneous solution. Addition of the oxirane (0.5 equiv.) causes immediate discharge of the colour, and after warming to 70 °C a copious white precipitate gathers (Scheme 1). The bis(diarylphosphine oxide) (**3**)† was isolated as a pure crystalline product [Ar^{1-4} = Ph; R^2 = H (75%), Me (84%), C_6H_4OMe-*p* (83%)] by acidification with dilute HCl, extraction with $CHCl_3$, concentration, and treatment with diethyl ether. The reaction does not appear to be affected by *ortho*-substituents on the phenyl ring(s) of the diarylphosphine oxide, but it is relatively sensitive to the number of substituents on the oxirane [$Ar^{1,3}$ = Ph; $Ar^{2,4}$ = C_6H_4OMe-*o*; R^2 = Me (81%)]. Interestingly, of the oxiranes that bear *adjacent* alkyl groups R^1 and R^2, only epoxycyclohexane gives the corresponding bis(phosphine oxide) [Ar = Ph (93%)]; *e.g.* 2,3-epoxybutane when allowed to react as described gave only the elimination product diarylphosphinic acid[3] *via* a cyclisation path, which in the case of a cyclohexane nucleus is precluded by the *trans* arrangement of the Ar_2PO– and NaO– fragments.[4]

Further, the presence of a polar organic solvent such as DMF seems to be crucial in the formation of the bis(phosphine oxides) (**3**) *via* this reaction sequence. Generation of the diarylphosphine oxide anion in tetrahydrofuran (THF) using n-butyl-lithium (16% solution in hexane) instead of sodium hydride, and addition of an oxirane gives, after work-up, only the 'half-product' (**4**), which is derived from ring opening. [Even when a ten-fold excess of the oxirane is employed, the reaction in THF gives (**4**) as the only product, with no subsequent polymerisation.] This product can be isolated, or allowed to react further with a second equivalent of the same (or a different) diarylphosphine oxide anion after replacement of THF by DMF. Thus the nature of the solvent exerts a larger influence on the course of the reaction than that of the base in generating the anion, and also provides an opportunity to prepare 'mixed' bis(phosphine oxides) in a sequential reaction, in one pot.

Oxiranes constitute an altogether simpler class of substrate than, for example, 1,2-bis(toluene-*p*-sulphonates) or dihalides in these 1,2-disubstitution reactions. Among the reaction pathways available to the intermediate (**2**) formed are cyclisation/elimination[3] and/or a retro-aldol type reaction.[5] Factors that are important in discriminating between these pathways, and therefore determine the synthetic scope of this method, will be presented shortly in a mechanistic study.

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† The structures of these compounds were established by elemental analyses and ^1H n.m.r., ^{31}P n.m.r., and methane chemical ionization mass spectra.

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