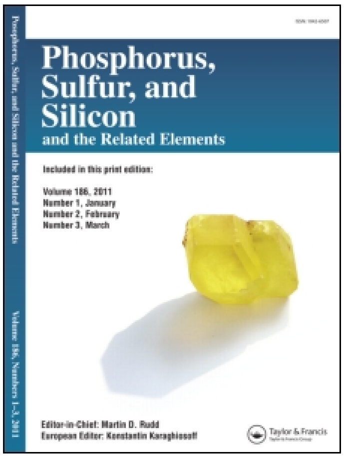

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The Reaction of the Diarylphosphine Oxide Anion with Oxiranes: A New Synthesis for 1,2-Ethanobis(Diaryl)Phosphines

Richard L. Wife[a]; Aart B. Van Oort[a]; Johannes A. Van Doorn[a]; Piet W. N. M. Van Leeuwen[a]
[a] Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B. V.), Badhuisweg 3, CM AMSTERDAM, The Netherlands

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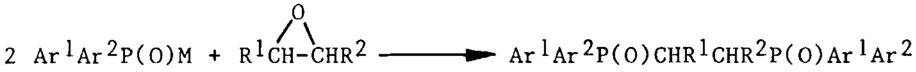
THE REACTION OF THE DIARYLPHOSPHINE OXIDE ANION WITH OXIRANES: A NEW SYNTHESIS FOR 1,2-ETHANOBIS(DIARYL)PHOSPHINES

RICHARD L. WIFE, AART B. VAN OORT, JOHANNES A. VAN DOORN and
PIET W.N.M. VAN LEEUWEN
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.),
Badhuisweg 3, 1031 CM AMSTERDAM, The Netherlands

Abstract The reaction of the diarylphosphine oxide anion with oxiranes gives bis-phosphine oxides in what is formally a double-substitution reaction but one which proceeds via a retro-aldol fragmentation and recombination process.

Bis-phosphines are used as bidentate ligands in a number of transition-metal-catalysed reactions. As part of our programme to investigate the influence of substituent groups in the close environment of the chelated metal centre, we have developed a synthetic method that affords variously substituted 1,2-bis(diaryl)phosphines. These are obtained directly by reduction of the corresponding oxides, which are prepared by double-substitution reactions using the anion Ar_2POM.[1] We now describe how the same anion can be reacted with the oxirane moiety to afford 1,2-bis-phosphine oxides in high yield, in an unusual double-substitution reaction.



$$2\ \mathrm{Ar^1Ar^2P(O)M} + \mathrm{R^1}\overset{\mathrm{O}}{\overbrace{\mathrm{CH{-}CH}}}\mathrm{R^2} \longrightarrow \mathrm{Ar^1Ar^2P(O)CHR^1CHR^2P(O)Ar^1Ar^2}$$

The anion is generated from the oxide $Ar_2P(O)H$ in N,N-dimethylformamide (DMF) by reaction with NaH (one equivalent), which gives a characteristically yellow homogeneous solution. Addition of the oxirane (half an equivalent) causes discharge of the colour and, upon warming of the solution to 70 ^{o}C, a copious white precipitate gathers. The bis(diaryl)phosphine oxides are isolated as pure crystalline products by acidification, extraction ($CHCl_3$), concentration and treatment with Et_2O. Ortho-substituents on the phenyl ring(s) of Ar_2PONa appear not to affect the high yield (> 80 %), but the reaction is relatively sensitive to the number of substituent groups contained in the oxirane. Further, the presence of a polar organic solvent such as DMF seems to be necessary for the sequence that affords the bis-phosphine oxide.

Generation of the anion Ar_2POLi in tetrahydrofuran (THF), using n-butyllithium (1.6 M in hexane) in place of NaH, and reaction with the oxirane give only the ring-opened "half-product". Even when a large excess of the oxirane is employed, this is the only product, and there is no subsequent polymerisation. The half-product can be isolated, or reacted further with a second equivalent of the same (or, indeed, a different) anion Ar_2POLi after replacement of the THF by DMF. Thus, the nature of the solvent exerts a larger influence on the course of the reaction than the metal cation from the base used to generate the anion.

Reaction of the oxirane with Ar_2POM (M = Na or Li) gives the expected trans- ring-opened intermediate (1), from which there are two divergent reaction pathways (Figure 1).

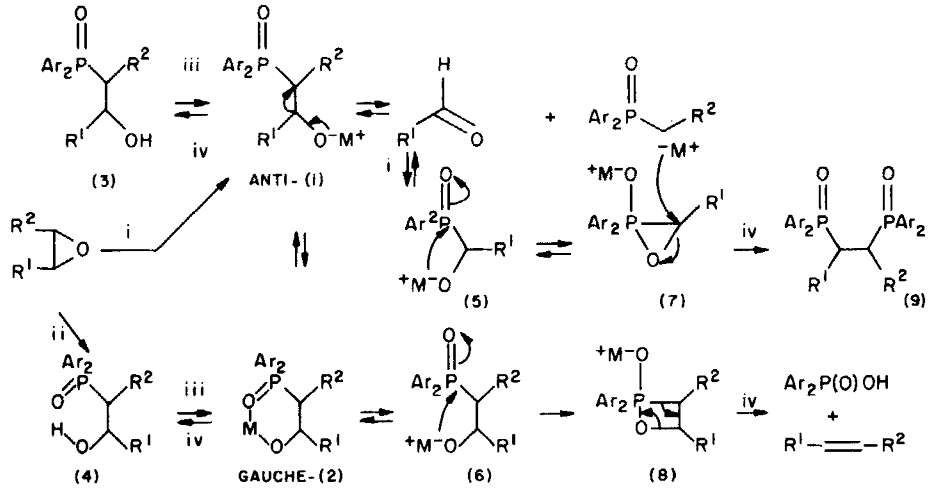


FIGURE 1 Reaction scheme. (Reagents: i, $Ar_2P(O)M$; ii, $Ar_2P(O)H$; iii, n-butyllithium; iv, H^+/H_2O.)

One results in the elimination of an olefinic product from the oxybetaine species (8) that is formed by cyclisation (6) of the gauche-conformer (2) of the intermediate, and is the second step of the Wittig-Horner reaction.[2,3] The other pathway gives the bis-phosphine oxide (9), the exclusive product derived from simple oxiranes on the further reaction of the ring-opened intermediate (1) with a second equivalent of Ar_2POM in polar aprotic solvents.

In the pathway to 9, the fragmentation[4] (a retro-aldol type reaction) of 1 appears to be crucial, and the interception of the aldehyde component by the second Ar_2POM equivalent generates an electrophilic adduct that reacts with the α-methylene anion in the final recombination step as shown (7). The withdrawal of aliquots during the early course of the reaction and their analysis (^1H-NMR and thin-layer chromatography) after work-up revealed substantial amounts of $Ar_2P(O)CH_3$ and an equal quantity of an as yet unidentified component that was neither the corresponding aldehyde fragment, nor the adduct derived from 5 by reaction with the second equivalent of Ar_2POM.[5]

This second equivalent of the anion clearly has a profound effect on the equilibrium process between 1 and 2, since the Wittig-Horner pathway is effectively closed. There are a number of reactions whereby a species such as 7 undergoes rearrangement,[6-8] resulting in the transfer of oxygen to the phosphinyl centre, but here the interception of 7 leads to 9 in a final recombination step. It is not altogether surprising that this pathway is sensitive to the number of substituent groups in the oxirane, as well as to their relative stereochemistries. A particularly dramatic illustration of the tight stereochemical control is found in the contrasting reactivities of the cis- and trans- intermediates of fixed stereochemistry derived from epoxycyclohexane. The cis-isomer (4; $R^1 = R^2 = -(CH_2)_4-$; the exclusive product obtained in 6 % yield from warming Ar_2POH in a solution of epoxycyclohexane at 130 °C for 2 hours under neutral conditions), when treated sequentially with

NaH and Ar_2PONa in DMF, undergoes elimination (Wittig-Horner reaction) even at room temperature. The trans-isomer (3; $R^1 = R^2 = -(CH_2)_4-$),[9] however, reacts further to give cleanly the trans-bisphosphine oxide product in 93 % yield. The fixed trans-gauche disposition of the P=O and ONa moieties precludes cyclisation to 8 (and thus elimination) but is suited[10] to the retro-aldol ring-opening, and the subsequent recombination of the activated fragments is assisted further by their covalent association.

The reaction pathways are finely balanced and by evaluation of the discreet steps it is possible to predict which pathway is dominant for a particular oxirane. Oxiranes constitute a simpler substrate for 1,2-double-substitution reactions than, for example, 1,2-ditosylates. The powerfully nucleophilic yet soft Ar_2PO^- anion is highly effective in a number of substitution reactions, and is a particularly versatile species in the construction of complex ligands.

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