

Phosphacycloprenes: The Synthesis of Triphenylphosphiren Oxide

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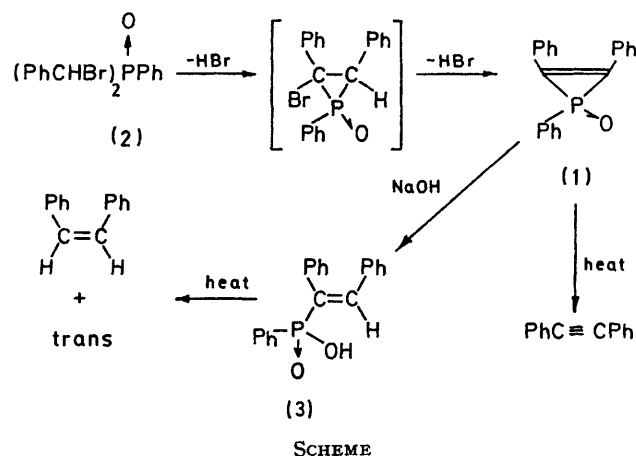
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Summary Triphenylphosphiren oxide has been prepared by the action of 1,5-diazabicyclo[4,3,0]non-5-ene (dbn) on bis-(α -bromobenzyl)phenylphosphine oxide.

HETEROCYCLOPROPENES are the simplest heterocycles which can conform to the Hückel rule ($4n + 2\pi$ -electrons) for aromaticity.¹ In addition to the number of π electrons in the closed system, however, the presence or absence of orbitals of suitable energy levels and orientation for π delocalization, the strain inherent in such small rings, and the size and electronegativity of the incorporated heteroatom² should be considered in assessing aromatic potential. In fact, the existence, either as stable molecules or as short-lived intermediates, of heterocyclopropenes containing boron,³ nitrogen,⁴ oxygen,⁵ silicon,⁶ sulphur,⁷ and germanium⁸ have been reported. We report the first evidence for the existence of triphenylphosphiren oxide (1), one member of a new class of potentially aromatic phosphacycloprenes.

A modification of the ring closure reaction effected by the action of base on substituted halomethylene sulphones, used as a general method in the synthesis of substituted thiiren dioxides, was employed in the preparation of (1).⁹ The addition of 1,5-diazabicyclo[4,3,0]non-5-ene (dbn) to a solution of bis-(α -bromobenzyl)phenylphosphine oxide† in benzene resulted in the immediate precipitation of dbn hydrobromide. Evaporation of the filtrate produced a light yellow oil which, after fractional reprecipitation several times from ether by pentane, was found to contain (1) contaminated with dbn hydrobromide.‡ Examination of this reaction product by g.l.c. showed the absence of bromostilbenes and diphenyl acetylene. In addition, treatment of bromo-

stilbene with dbn under the reaction conditions did not afford diphenyl acetylene. Compound (1) gave a mass spectrum showing a parent ion at m/e 302 and diphenylacetylene, 178. The ¹H n.m.r. spectrum (external Me₄Si) showed complex multiplets at δ 7.1–7.9 (Ph) and δ 1.8–3.8 p.p.m. (dbn). The i.r. spectrum of (1) showed a band at 7.9μ (P=O) and there were absorption maxima in the u.v. at 274 and 282 nm as well as broad absorption up to 310 nm. Pyrolysis of (1) at 120° at 10^{-5} – 10^{-6} Torr gave



diphenylacetylene. The addition of aqueous sodium hydroxide to (1) afforded 1,2-diphenylvinylphosphinic acid (3) (75%) (m.p. 160–163°), ¹H n.m.r. (CDCl₃), δ 7.1–7.6 (16H, aromatic), 12.5 p.p.m. (1H, acid); P n.m.r., broad

† Compound (2) was obtained by the bromination of dibenzylphenylphosphine oxide. Although column chromatography could be used to separate *meso*-(2) from the (\pm)-pair, the reaction of each diastereomer was the same, so that the mixture of isomers was routinely used.

‡ Anal. calc. for (1), C 79.5%: found (after subtraction of DBN, HBr present as determined by N and n.m.r. analysis), 79.0%. Elemental analysis and integration of the n.m.r. spectrum indicated the same ratio of (1) and dbn. All other compounds gave satisfactory analysis.

peak 30.6 ± 0.5 p.p.m. The mass spectrum showed a parent peak at m/e 320, and peaks for the loss of water at 302, and for diphenylacetylene at 178.

Pyrolysis of (3) yielded *cis*- and *trans*-stilbenes in about a 3:1 ratio as the only volatile products. Attack of (1) at phosphorus by water should give only the *cis* ring-opened product since collapse of the carbanion should be fast compared to rotation to give *trans*-products.¹⁰ The formation of the large proportion of the thermodynamically unfavoured *cis*-stilbene in the pyrolysis of (3) indicates that it is predominantly the *cis*-isomer. When water was not carefully excluded from the reaction of (2) with dbn, (3) was obtained directly.

These data are most consistent with a reaction sequence that involves the elimination of hydrogen bromide from (2) to form the phosphiran oxide intermediate which undergoes subsequent 1,2-elimination to afford triphenylphosphiren oxide (1).¹¹ We favour a 1,3-elimination mechanism (as opposed to carbene formation followed by insertion) for the formation of the phosphiran oxide intermediate (Scheme).

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