A Novel Phosphorus → Oxygen Phenyl Migration: Triphenylphosphine Dioxide as a Reaction Intermediate

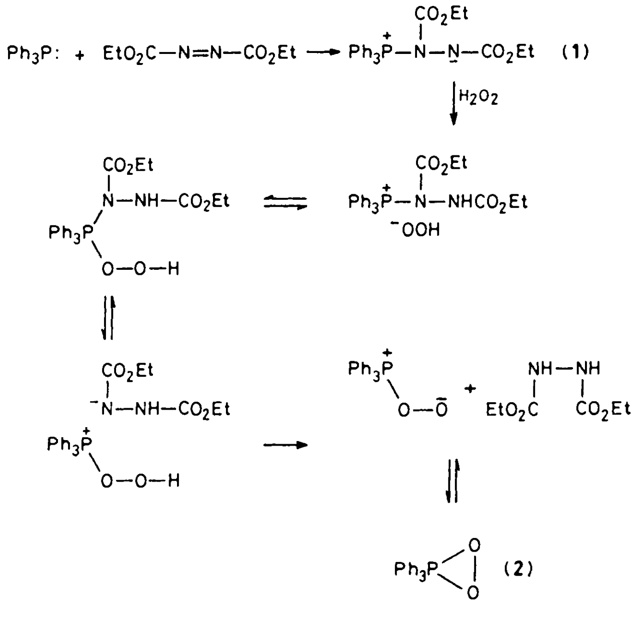
Mark von Itzstein and Ian D. Jenkins*

School of Science, Griffith University, Nathan, Queensland, 4111, Australia

Treatment of triphenylphosphine with diethyl azodicarboxylate and hydrogen peroxide results in the formation of phenyl diphenylphosphinate; triphenylphosphine dioxide is suggested as an intermediate.

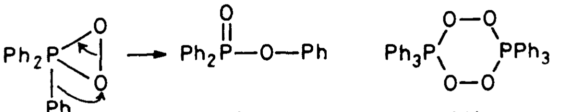
Triphenyl phosphite ozonide, $(PhO)_3PO_3$, is a useful reagent in organic synthesis as a source of singlet oxygen, $^1O_2$ [though in some cases $(PhO)_3PO_3$ and $^1O_2$ give slightly different results].[1,2] Although the corresponding triphenylphosphine ozonide has not been prepared, it is probably formed *in situ* and undergoes immediate loss of oxygen to give triphenylphosphine oxide.[3] We required, not a source of singlet oxygen, but a source of 'oxene'[4,5] or atomic oxygen (O:) and considered that the previously unknown triphenylphosphine dioxide, Ph_3PO_2, might lose 'oxene' to give triphenylphosphine oxide in a similar manner.

Treatment of triphenylphosphine with diethyl azodicarboxylate and alcohols (ROH) in chloroform or tetrahydrofuran results in the formation of phosphoranes, $Ph_3P(OR)_2$.[6] It was argued that replacing the alcohol by hydrogen peroxide should result in the formation of triphenylphosphine dioxide (**2**) as shown in Scheme 1. When the betaine (**1**) from triphenylphosphine and diethyl azodicarboxylate was treated with hydrogen peroxide at 0 °C, there was no evidence of phosphorane formation by ^{31}P n.m.r. spectroscopy and instead of the expected triphenylphosphine dioxide or its decomposition product triphenylphosphine oxide (which was a minor product) the major product formed was phenyl diphenylphosphinate (**3**). It is difficult to account for the formation of this product other than *via* a rearrangement of triphenylphosphine dioxide (**2**) [or of its dimer (**4**)] as shown in Scheme 2.



Scheme 1

An analogous phenyl migration from phosphorus to oxygen occurs during the thermal rearrangement of bis(diphenylphosphinic) peroxide.[7] Phosphorus to carbon phenyl migrations are well known[8] but phosphorus to oxygen migrations are much less common. Interestingly, when hydrogen peroxide was replaced by *t*-butyl hydroperoxide, the phosphorane $Ph_3P(OOBu^t)_2$ was formed as shown by the high-field absorption [−42.3 p.p.m.($CHCl_3$)] in the ^{31}P n.m.r. spectrum and by analogy with other work.[6] This phosphorane decomposed rapidly at room temperature to give triphenylphosphine



(3) (4)

Scheme 2

oxide, but its observation lends some support to the proposed formation of (**2**) (Scheme 1).

The triphenylphosphine oxide formed during the reaction of the betaine (**1**) with hydrogen peroxide appears to be the result of a side-reaction of the proposed intermediate (**2**), namely oxidation of the diethyl hydrazinedicarboxylate back to the azo-compound. This side-reaction becomes the major reaction when triphenylphosphine is replaced by tributylphosphine. Thus, treatment of tributylphosphine with diethyl azodicarboxylate followed by hydrogen peroxide resulted in the immediate formation of tributylphosphine oxide and diethyl azodicarboxylate as the only products detected. Neither tributylphosphine nor the azo-compound were present prior to the addition of hydrogen peroxide, and diethyl hydrazinedicarboxylate was not oxidised to the azo-compound by hydrogen peroxide under the reaction conditions.

The rearrangement of triphenylphosphine dioxide to phenyl diphenylphosphinate (Scheme 2) is reminiscent of the Baeyer–Villiger oxidation of ketones to esters. However, attempted Baeyer–Villiger oxidation of triphenylphosphine oxide with *m*-chloroperbenzoic acid or with hydrogen peroxide–trifluoroacetic acid–trifluoroacetic anhydride was unsuccessful, the oxide being recovered unchanged.

In conclusion, an interesting rearrangement reaction in organophosphorus chemistry is reported and a mechanism involving the intermediate formation of triphenylphosphine dioxide is suggested.

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