The Mechanism of the Rearrangement of Bis-(diphenylphosphinyl) Peroxide

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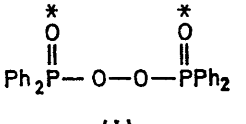
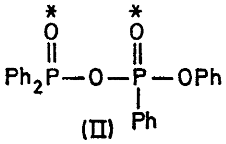
Summary The thermal rearrangement of bis-(diphenylphosphinyl) peroxide (I), labelled with ^{18}O on the oxo-oxygen atoms, to the unsymmetrical anhydride (II) proceeds with retention of ^{18}O in these positions.

PREVIOUS work has shown that the peroxide (I) decomposes to give a high yield of the corresponding anhydride (II) by a heterolytic mechanism with first-order kinetics.[1] It is now found that on rearrangement of a sample with ^{18}O-labelled oxo-oxygen atoms, the isotope remains in these positions.

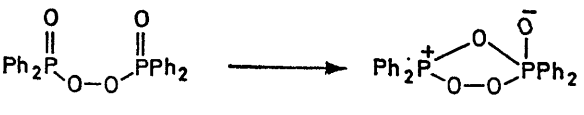

(I)


(II)

The analysis, to be described in detail elsewhere, was performed in the following way. Hydrolysis of (II) gave *O*-phenyl hydrogen phenylphosphonate, which gave phenol on treatment with sodium–naphthalene. The phenol, converted into the trimethylsilyl ether, contained no detectable ^{18}O. Mass spectroscopic analysis of the product gave, in addition to the principal peak (*m/e* 434) of the unsymmetrical anhydride, a peak of *m/e* 233 corresponding to $PhP(:O)(OPh)O^+$. Comparison of this with the 235 peak showed that only one ^{18}O atom was incorporated in each molecular ion. This means that the other ^{18}O atom must be in the $Ph_2P{=}O^*$ fragment.

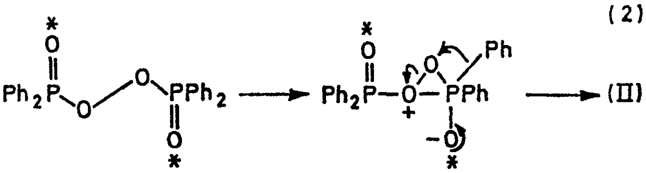
To establish the isomer distribution completely, the product was treated with methanol to give *O*-methyl *O*-phenyl phenylphosphonate. Comparison of the *m/e* 248 and 250 peaks of this ester showed the presence of one labelled oxygen atom only† ($3{\cdot}8 \pm 0{\cdot}4\%$ ^{18}O *cf.* $4{\cdot}6\%$ theoretical). This ^{18}O oxygen atom must be the oxo-oxygen atom, since the methoxy-group comes from the [^{16}O]methanol and we have already found that the phenolic oxygen atom is not labelled.

This remarkable result shows that previously postulated mechanisms,[1] involving attack by the phosphinyl oxygen atom on the second phosphorus atom, are not correct, *viz.*


(1)

reaction (1). This reaction may be prevented by the strain generated at the phosphonium centre, with phosphorus in a 5-membered ring.[2] Similarly a dissociative process (ionic or radical) is an unlikely one, as this should lead to extensive scrambling of the ^{18}O isotope.[3]

The mechanism thus appears to be intramolecular, involving the interaction of one of the peroxy-oxygen atoms with the phenyl group, the other at the second phosphorus atom, *viz.* reaction (2). The nucleophilic reactivity of the


(2)

peroxy-oxygen atom may be enhanced by lone-pair–lone-pair repulsions[4] (the "α-effect"), and mechanisms of this kind involving 3-membered cyclic intermediates have been frequently postulated to explain rearrangements of phosphorus compounds.[5]

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† The limited accuracy of this measurement is due to the relatively weak intensities of these peaks.

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[2] C. Brown, R. F. Hudson, V. T. Rice, and A. R. Thompson, *Chem. Comm.*, 1971, 1255.
[3] D. B. Denney, *J. Amer. Chem. Soc.*, 1956, **78**, 590.
[4] J. D. Aubort and R. F. Hudson, *Chem. Comm.*, 1970, 937.
[5] P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, 1965, **21**, 1961.