Ozonolysis of Bis[tris(trimethylsilyl)methyl]diphosphene

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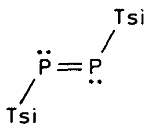
Ozonolysis of the diphosphene (**1**) occurs with a 2 : 1 stoicheiometry (ozone : diphosphene); the reaction, carried out at low temperature, gives a relatively stable cyclic diperoxide (**2**).

Diphosphenes have been of current interest since their discovery in 1981,[1] both from a theoretical and a synthetic point of view,[2–4] but little is known about their reactivity.[1,2,5] We have now studied the reactivity of a very powerful oxidative reagent (ozone) with this new class of unsaturated model compound. The bis[tris(trimethylsilyl)methyl]diphosphene (**1**)[4] does not react with ground-state oxygen, water, or methanol at room temperature, but reaction with ozone occurs rapidly and quantitatively, even at low temperature.

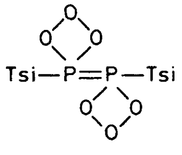
Ozonization of (**1**) was carried out at −80 °C in toluene until the initial pink colour of the solution had disappeared. Iodometric titration of unchanged ozone indicated a 2:1 (ozone : diphosphene) stoicheiometry. The solution, purged with argon, was then studied by ^{31}P n.m.r. spectroscopy at low temperature. The signal corresponding to (**1**) [$\delta(^{31}\text{P}) = +598$ p.p.m. relative to ext. 85% H_3PO_4] completely disappeared and was replaced by a single signal [$\delta(^{31}\text{P}) = +33$ p.p.m.] corresponding to (**2**).

The product (**2**) is relatively stable, since we have observed it up to +40 °C, allowing its mass spectrum to be studied: $(M-1)^+$, *m/z* 619. This value indicates that both ozone molecules have become bonded to the diphosphene (**1**), so (**2**) corresponds to the formula $(\text{TsiPO}_3)_2$. This excludes a metaphosphonate structure –P(:O)(:O) which we obtained by ozonolysis of bis(2,4,6-tri-t-butylphenyl)diphosphene.[6]

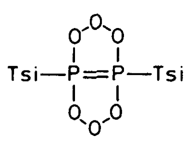
The product (**2**) could have various structures (**2a—d**), and we have studied some specific reactions in order to characterize it. By analogy with phosphite ozonides $\geqslant\overline{\text{P}\cdot\text{O}\cdot\text{O}\cdot\text{O}}$,[7] (**2a**) ought to give singlet oxygen when it decomposes. So we added a specific acceptor of singlet oxygen (9,10-diphenyl anthracene) to a solution of (**2**), but we did not obtain the corresponding endoperoxide. Moreover, for structures (**2a**) and (**2b**) the phosphorus–phosphorus double bond is not broken; this is unlikely in reaction with ozone. The structures (**2b**) and (**2c**) can also be ruled out, because tetracyanoethylene, which is oxidized by O–O–O linkages but not by



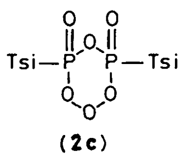
(1)



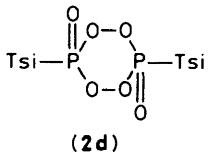
(2a)



(2b)



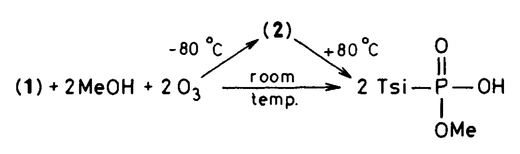
(2c)



(2d)

Tsi = $(Me_3Si)_3C$

$$2Bu_3P \xrightarrow{(2)} 1.75Bu_3P(:O) + 0.25Bu_2P(:O)OBu \qquad (1)$$



$$(1) + 2MeOH + 2O_3 \xrightarrow[\text{temp.}]{\text{room}} 2\ Tsi\text{—}P(=O)(OMe)\text{—}OH \qquad (2)$$

(3)

peroxides,[8] does not react with (2). At room temperature, one molecule of (2) is able to oxidize *two* molecules of tributylphosphine, showing that it is a good oxidative reagent. [Reaction (1).]

Oxidation of phosphines is a common method for titration of peroxidic bonds,[9] so (2) must have two peroxidic bonds. Furthermore the side formation of dibutyl phosphinate indicates a radical reaction.[10] According to these reactions, the only plausible structure for (2) seems to be the cyclic diperoxide (**2d**).

If ozonization of (**1**) is carried out in the presence of methanol at low temperatures, the only product obtained is again (**2**), which does not react with methanol. However, heating this solution for 2 days at +80 °C gives the monoester (**3**) (80% yield). When ozonization is carried out at room temperature in MeOH–toluene (40:60), the same monoester (**3**) is obtained quantitatively [^{31}P n.m.r. δ +37 p.p.m. ^1H n.m.r. (toluene) δ 0.4 (27H, s) and 3.6 (3H, d, $^3J_{OMe}$ 11 Hz). Field desorption mass spectrum, M^+, *m/z* 326]. [Reaction (2).]

Hence ozonization of the diphosphene (**1**) does not give ozonides as do phosphites or alkenes. However, (**2**) is analogous to cyclic diperoxides,[11] and (**3**) to esters which are often obtained on ozonization of alkenes.[8]

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