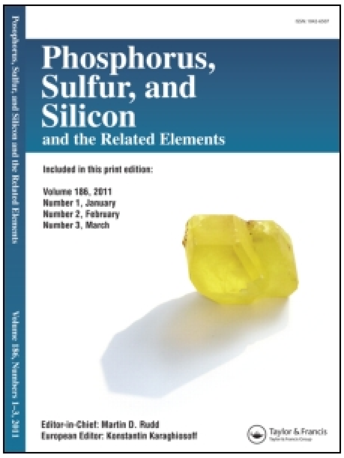

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CYCLIC ORGANOPHOSPHORUS COMPOUNDS. PART XV.[1] 4-t-BUTYL-2,6,7-TRIOXA-1-PHOSPHABICYCLO[2,2,2]OCTANE AND ITS OXIDE

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Treatment of 4-*t*-butyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane with sulphuryl chloride yields merely its P-oxide and not the expected 5-*t*-butyl-2-chloro-5-chloromethyl-1,3,2-dioxaphosphorinan 2-oxide. The mass spectra of the bicyclic phosphite and its oxide are discussed.

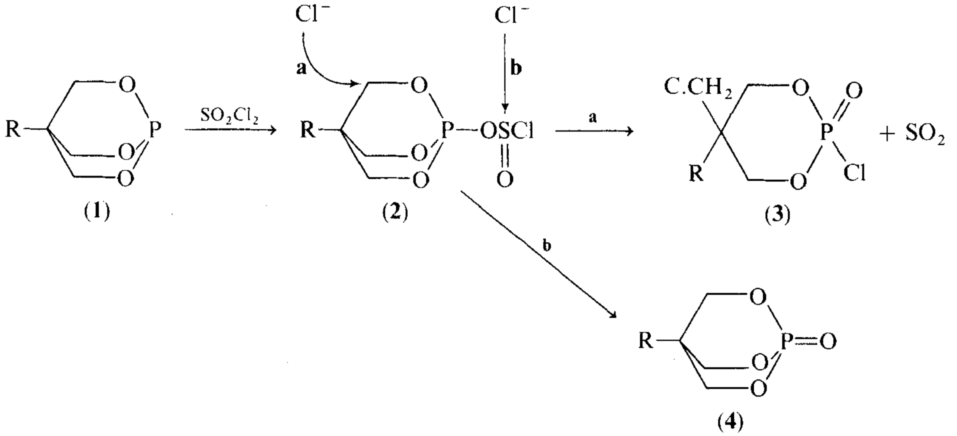
The 2,6,7-trioxa-1-phosphabicyclo[2,2,2]octanes (**1**; R = Me or Et) readily undergo stereospecific ring opening on treatment with elemental chlorine or bromine, or with sulphuryl chloride, to yield the 2-halo-5-halomethyl-5-methyl-1,3,2-dioxaphosphorinan 2-oxides (**3**; R = Me or Et).[2] Variable amounts of the corresponding 2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane 1-oxide are also formed, the yields of these being dependent upon the reaction solvent and are greater when diethyl ether rather than ethanol-free chloroform is used.[3]

We now report the synthesis (see experimental) of the *t*-butyl compound (**1**; R = Bu^t) via the hitherto unrecorded 1,1,1-tri(hydroxymethyl)-2,2-dimethylpropane, so completing the availability of members of the series (**1**; R = H, Me, Et, Pr^i, and Bu^t. When the bicyclic phosphite was treated with sulphuryl chloride under conditions under which the compounds (**1**; R = Me or Et) yield no P-oxide, the sole product was the P-oxide (**4**; R = Bu^t) and not the phosphorochloridate (**3**; R = Bu^t).

Thus the *t*-butyl group offers a marked steric resistance to nucleophilic ring opening (**2**; pathway a) resulting in highly selective reaction at sulphur (Scheme I).[4]

We have previously observed the failure to ring open in the case of reactions between the nitro phosphite (**1**; R = NO_2) and alkyl halides, even reactive benzylic halides, in the normal Arbuzov reaction.[3] This could be the result of low electron density at phosphorus and of reduced nucleophilic character, and is an effect also found in acyclic phosphites possessing electron attracting groups on carbon.[15]

The mass spectrum of the bicyclic phosphite (Scheme II) possesses a marked molecular ion peak at m/e 190 (55 %). Loss of the *t*-butyl radical



SCHEME I

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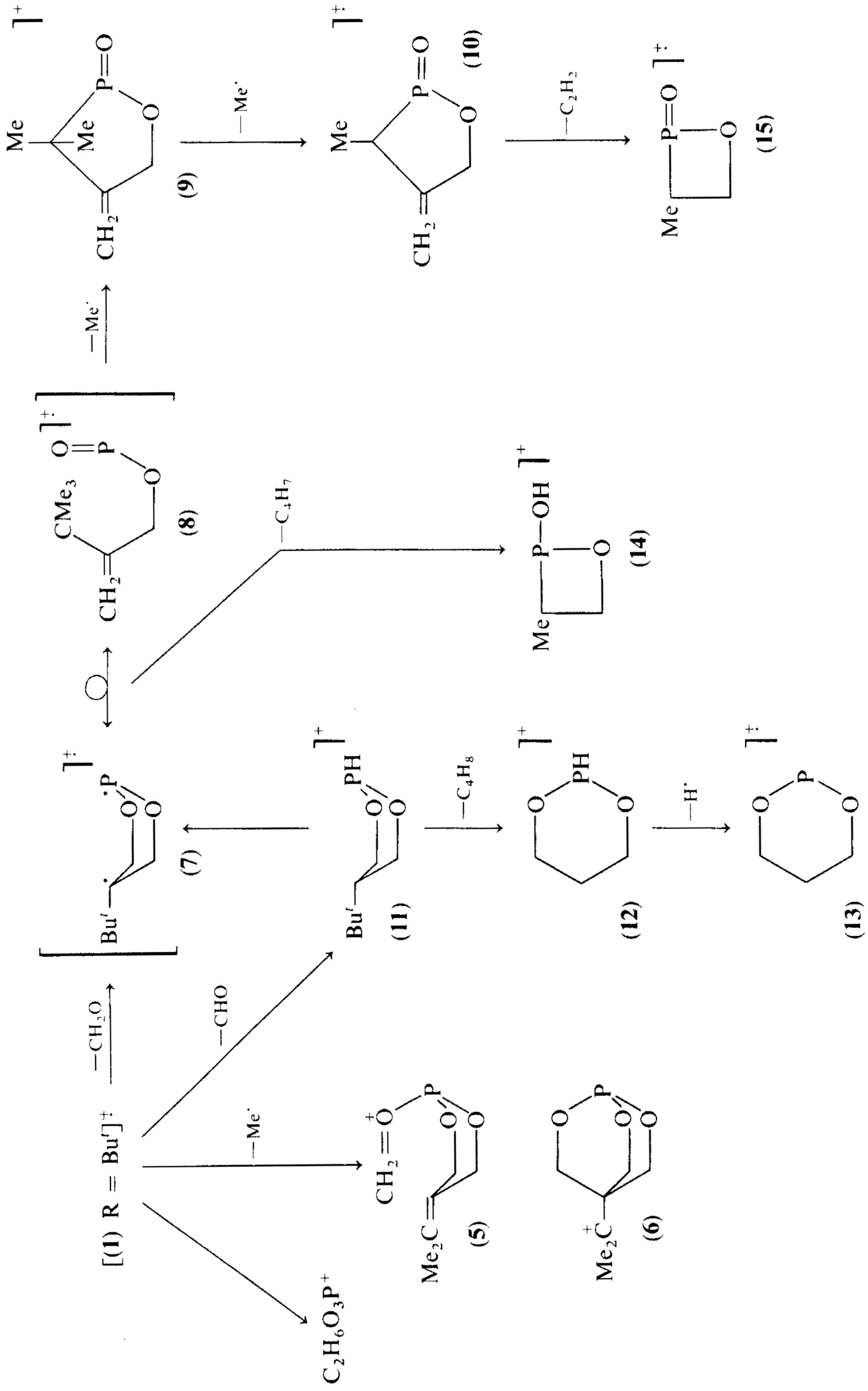
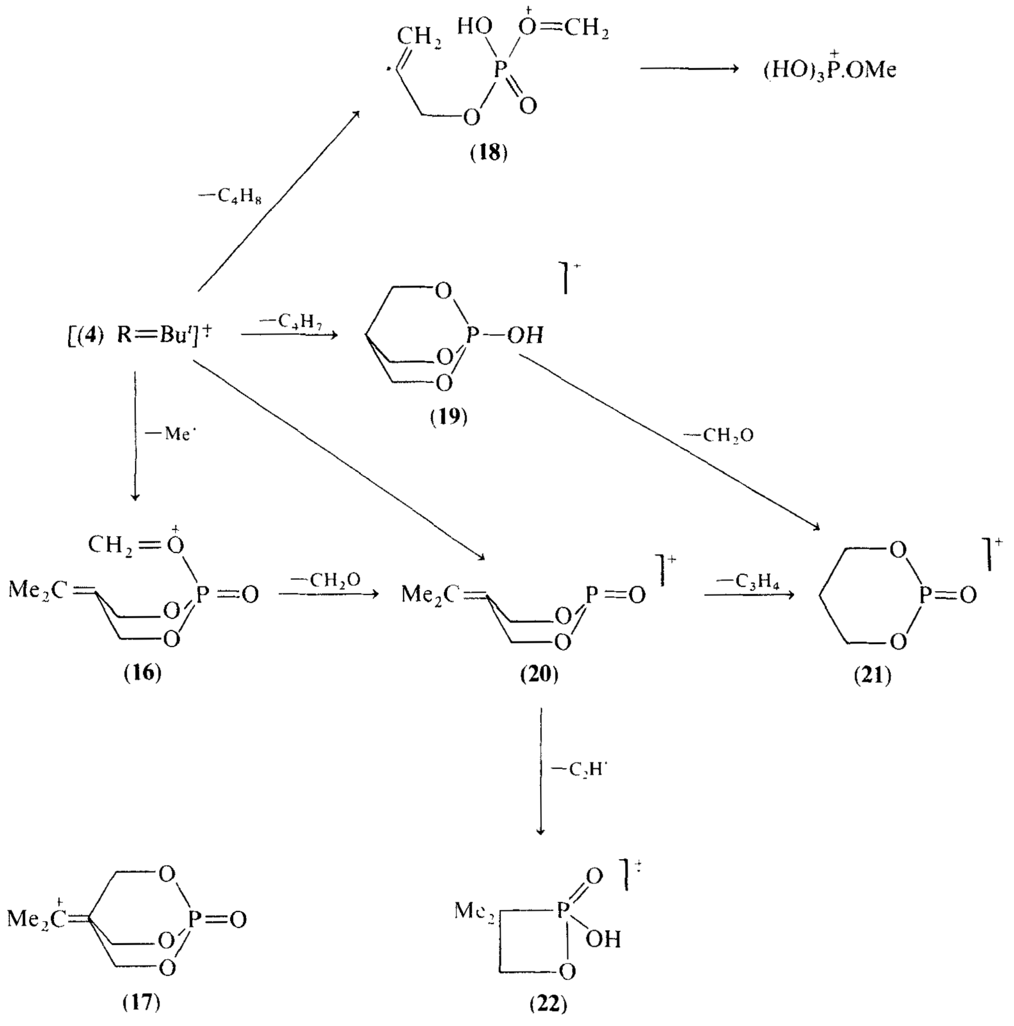

[(1) R = Bu^t]$^{+\cdot}$
$C_2H_6O_3P^+$
—Me$^\cdot$
—CHO
—CH$_2$O
(5)
(6)
(7)
(8)
—Me$^\cdot$
(9)
—Me$^\cdot$
(10)
—C_2H_2
(15)
—C_4H_7
(14)
(11)
—C_4H_8
(12)
—H$^\cdot$
(13)

SCHEME II

to give the cation of m/e 133, or of isobutene to give the ion radical of m/e 134, are not observed. However, traces of the M–15 ion, of possible structure (**5**) or (**6**), are apparently formed. The main degradative pathway appears to be via loss of formaldehyde from the molecular ion to give the important m/e 160 fragment, for which the alternative formulations (**7**) and (**8**) are depicted. Sequential decay of this species to an ion of m/e 145 (**9**; 4%) is suggested by the presence of the metastable at 131.3 (cal. 131.4); further decay leading to the ion of m/e 130 by loss of methyl, is more likely than formation of the latter ion by loss of two formaldehyde molecules from the m/e 160 ion. Two other initial degradation steps for the molecular ion are of minor importance; they are direct formation of the ion at m/e 109 ($C_2H_6O_3P^+$) as evidenced by the metastable at 62.5 (cal. 62.5), and the apparently direct formation of the fragment (**11**) of m/e 161, presumably by loss of CHO from M^+. The ion (**11**) could, in turn, lead to the m/e 160 ion, but its importance, although evidently secondary to that of the m/e 160 ion, seems to lie in its degradation to the m/e 105 ion (**12**) by loss of isobutene, consistent with the metastable at 68.4 (calc. 68.5); presumably ion (**12**) is the source of the m/e 104 ion (**13**).

The presence of the m/e 109 (12%) and m/e 83 ($C_5H_7O^+$; 98%) ions in the spectra of other bicyclic phosphites has been accounted for by assuming degradation of the ion m/e 131 ($C_5H_8OP^+$);[6] in the present case, the latter ion is



SCHEME III

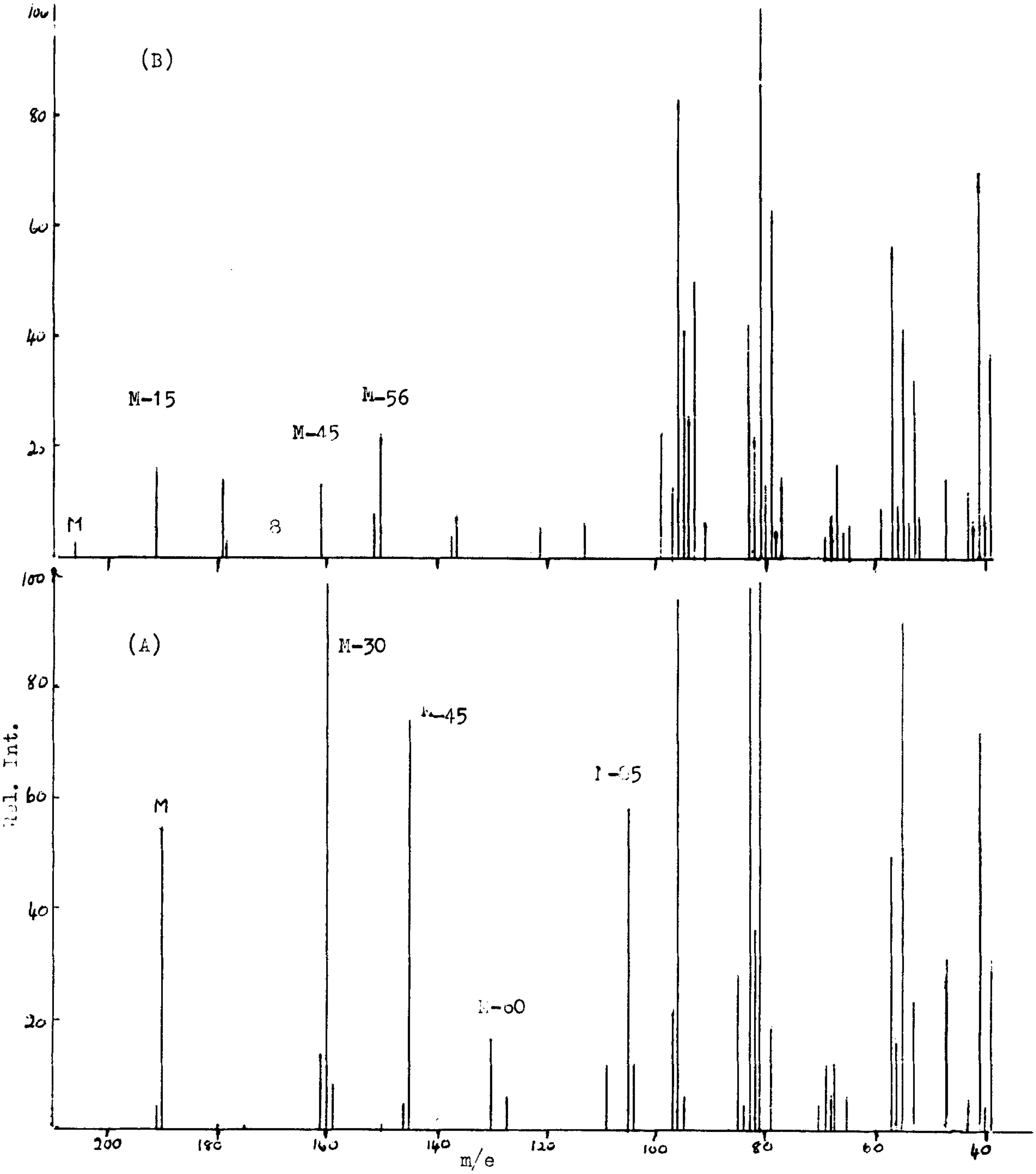


FIGURE 1 Mass spectra of (A) 4-*t*-butyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane, and (B) 4-*t*-butyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane 1-oxide.

absent, and as seen already, the molecular ion is the more likely source.

The possible involvement of 1,2-oxaphosphetan ions in the mass spectrometric degradation of bicyclic phosphites has been suggested by Hendricker,[6] and also for monocylic 1,3,2-dioxaphosphorinans by others.[7] In particular, Hendricker suggested the formation of a 1,2-oxaphosphetan ion of m/e 103 from the methyl and ethyl bicyclic phosphites via the appropriate ions analogous to **(7)** or **(8)**. In the present case, the m/e 103 ion is absent, as is a structurally related ion of m/e 130 reached by loss of CH_2OH from **(11)**. However, in addition to the representations of the m/e 104 and 105 ions as 1.3.2-dioxaphosphorinan ions, already referred to, alternative formulations might be the 1,2-oxaphosphetan structures **(14)** and **(15)** respectively.

A cursory glance at the spectra (Figure 1) of the phosphite and phosphate indicates the fundamental difference in stability of the higher mass ions. Both compounds provide a complex pattern of degradation fragments with masses < 100 a.m.u.

The molecular ion of the phosphate (Scheme III) is very weak, with the M-15 ion **(16** or **17)** being of much greater importance than for the phosphite. Direct loss of formaldehyde from the molecular ion is not evident. Loss of isobutene from the molecular ion leads to the m/e ion **(18)** whilst loss of C_4H_7 accounts for the presence of an ion of m/e 151 **(19)**. A synchronous loss of methyl and formaldehyde, i.e. total 45 a.m.u., also from the molecular ion, would explain the occurrence of an ion having m/e 161, and formulated as **(20)**. The participation of ions such as **(18)** carrying a single carbon atom on oxygen, is suggested by the subsequent formation of the weakly present m/e 113 species, thought to be $MeOP(OH)_3^+$.

Loss of C_3H_4 from **(20)**, or from a structural isomer thereof, leads to what is probably a 1,3,2-dioxaphosphorinan ion **(21)** of m/e 121. The ion of m/e 136 ($C_4H_9O_3P$) depicted as the 1,2-oxaphosphetan acid ion **(22)** is most probably derived from **(20)** by loss of $C_2H^{\cdot}$.

EXPERIMENTAL

M.ps. are uncorrected. Infrared spectra were determined for films or KBr discs using an Infracord 257 spectrometer, and 100 MHz ^1H n.m.r. spectra were determined for $CDCl_3$ solutions (Me_4Si as internal standard) using a Jeol JNM-MH-100 instrument. Mass spectra were obtained using the A.E.I. MS-903 instrument operating at 70 ev. Accurate mass measurements were performed on several ions; the results are listed in Table I.

TABLE I

Accurate mass determination

Fragment m/e	Structure	Found	Calc.
Bicyclic phosphite			
96	C_7H_{12}	96.09332	96.09389
109	$C_2H_6O_3P$	109.00512	109.00545
160	$C_7H_{13}O_2P$	160.06562	160.06530
Bicyclic phosphate			
96	C_7H_{12}	96.09540	96.09390
136	$C_4H_9O_3P$	136.02891	136.02892
161	$C_6H_{10}O_3P$	161.03611	161.03674

1,1,1 - Tri(hydroxymethyl) - 2,2 - dimethylpropane This was prepared by base-catalysed reaction between formaldehyde and 3,3-dimethylbutanal. The latter, b.p. 102–105°C, ν_{max} 1724 (C=O) cm^{-1}, was obtained either by ozonolysis of 4,4-dimethylpent-1-ene, b.p. 68–72°/740 mm, when the yield was 68%, or more conveniently by initial hydroxylation of the alkene with formic acid–25% hydrogen peroxide to give 1,2-dihydroxy-4,4-dimethylpentane, b.p. 83–86°/1 mm, in 45–65% yield, followed by cleavage of the latter by periodic acid in aqueous 30% methanol, when the yield of aldehyde was 70%.

Calcium oxide (13.3 g) was added in portions to a stirred mixture of 3,3-dimethylbutanal (35 g) and 37–40% aqueous formaldehyde (120 g) at <40°C; the mixture was then stirred at ambient temperature for 3 h, then at 70–80°C for 35 h, and the brown solution was then extracted continuously with ether to give the *triol* (13.1 g, 23%), m.p. 238–239°C (from carbon tetrachloride), ν_{max} 3720 cm^{-1}. (Found: C, 58.9; H, 11.0. $C_8H_{18}O_3$ requires C, 59.24; H, 11.18%). The *tri-p-nitrobenzoate*, m.p. 135–137°, crystallizes from ethanol. (Found: N, 6.4. $C_{29}H_{27}N_3O_{12}$ requires N, 6.89%).

4 - t - Butyl - 2,6,7 - trioxa - 1 - phosphabicyclo[2,2,2]octane A mixture of the above triol (7.5 g), freshly distilled triethylphosphite (7.5 g) and triethylamine (5 drops) was slowly heated when ethanol (66%) distilled. Sublimation of the solid residue at 240–250°C afforded the bicyclic *phosphite* (6.5 g, 79%). m.p. 144–149°C. A sample m.p. 149–151°C (from chloroform-light petroleum, b.p. 60–80°) showed ν_{max} 992 (POC) cm^{-1}; δ 0.90 (s, 9H), 4.08 (d, 6H, J_{POCH} 2.2 Hz) p.p.m. (Found: C, 50.4;H, 7.95. $C_8H_{15}O_3P$ requires C, 50.53; H, 7.95%).

Chlorination of 4-t-butyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]-octane A solution of redistilled sulphuryl chloride (4.3 g) in dry ethanol-free chloroform (15 ml) was added dropwise to one of the phosphite (5.9 g) in the same solvent (35 ml). When the exothermic reaction had subsided, the solution was allowed to stand for 2 h, and then evaporated to a solid (5.5 g, 86%), m.p. 290–305°C, shown to be *4-t-butyl-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]octane 1-oxide*, m.p. 321–324° (from benzene), ν_{max} 1312 (P=O), 990, 976 (POC) cm^{-1}, δ 0.96 (s, 9H), 4.63 (d, 6H, J_{POCH} 7.2 Hz) p.p.m. (Found: C, 46.48; H, 7.2. $C_8H_{15}O_4P$ requires C, 46.60; H, 7.33%).

There were no indications of the formation of the cyclic phosphorochloridate (3; R = Bu′).

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