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8-PHOSPHABICYCLO[3.2.1]OCTANES—III[4]

THE REACTION BETWEEN OXYALLYL CATIONS AND PHOSPHOLE DERIVATIVES

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Abstract—The reaction of oxyallyl cations with phosphole sulfide as well as phosphole oxides was investigated and was found to give the expected 8-phosphabicyclo[3.2.1]octanic system (**2**, **4** and **7**) apart from other unexpected products (**3** and **5**).[1] In the case of the phosphole sulfide (**1**), the oxyallyl cation is believed to react preferentially with the P=S group, rather than the dienic moiety, leading to a P=S to P=O transformation or to a very particular reaction resulting in **5**. This occurs through an intermediate (**j**) in which a C=S group reacts in a [2 + 4] cycloaddition with the phosphole as a diene. The structure and stereochemistry of the various products were established by the aid of their spectral data in conjunction with spectral data of some related compounds. A formal PhPO extrusion occurs while reacting compound **5**, or a model compound, with *m*-chloroperbenzoic acid. This PhPO elimination is believed to occur through an intermediate phosphinate resulting from Bayer-Villiger like oxidation, which then loses the [$PhPO_2$] group.

Phosphole sulfide (**1**), previously found to react as a dienophile, was shown to enter a [2 + 4] cycloaddition as a diene with powerful dienophiles like 4-methyl-1,2,4-triazoline-3,5-dione (**10**).

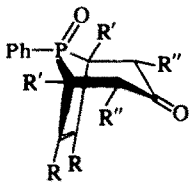
The cycloaddition of oxyallylic cations to conjugated dienes (cyclopentadiene, furane, N-methylpyrrole etc) have been shown to offer an efficient and general tool for the construction of bicyclo[3.2.1]octanes, as well as the corresponding 8-oxa- and 8-azabicyclic systems.[1]

In the course of our investigation of the 8-phosphabicyclo[3.2.1]octanic system,[2-4] it was interesting to investigate whether the above synthesis could also be further expanded for the preparation of these compounds i.e. reacting phospholes, as dienes, with the oxyallyl cation. The phospholic systems are known as poor dienes, though the oxides, e.g. 1-phenyl-1-oxo-3,4-dimethylphosphole (**8**), are at least as good as cyclopentadiene and undergo rapid dimerization.[5] The thio analog of the oxide **8** (compound **1**) can also be utilized in Diels–Alder reactions. In contrast to the oxide, the phosphole sulfide does not undergo dimerization[6] and has already been used by us in cycloaddition reactions.[7] Indeed, in the reaction of 1-phenyl-1-thio-3,4-dimethylphosphole (**1**) with tropone,[7] compound **1** reacted as the dienophile rather than the diene, in a [4+2] cycloaddition reaction. Nevertheless, we thought it worthwhile to check the reactivity of compound **1** towards the much more reactive oxyallylic cation.

The reaction between compound **1** and the oxyallyl cation, the latter prepared by the addition of Zn(Cu) couple to a solution of 2,4-dibromo-3-pentanone in dry glyme,[8] led to the isolation of two compounds **2** and **3** in 40% and 60% yield respectively.

Compound **2**, according to the NMR spectrum (Table 1) was an expected adduct of both reactants, namely a 8-phosphabicyclo[3.2.1]octane system. However it did not contain the P=S moiety but a phosphoryl one, as was confirmed by the IR spectra (1200 and 1170 cm^{-1} (P=O)), elemental analysis ($C_{17}H_{21}O_2P$) and mass spectrum (*m/e* 288; M^+). the second compound (**3**) turned out to be the dimer of 1-phenyl-3,4-dimethylphosphole oxide[6] (**8**)—again a product of the phosphole oxide rather than the sulfide. The question arises as to whether the phosphole sulfide can react in this cycloaddition reaction, to give compound **2**, or whether it is initially converted to the oxide which then competetively gives the bicyclo[3.2.1]octanic system or the dimer. Carrying out the synthesis, with the more stable dibenzyl-oxyallyl cation prepared under other conditions (by reacting α,α'-dibromodibenzyl ketone with NaI in boiling CH_3CN[9]) resulted once again in two phosphoryl bearing compounds (**3** and **4**) but in much lower yields, when compared with the above reaction, with Zn(Cu), to give **2** and **3**. Furthermore a third compound (**5**) was isolated in varying yields (3% to 30%) depending on the reaction conditions. The spectral data of compound **4** (Table 1 and Experimental) proves its structure as another 8-phosphabicyclo[3.2.1]octane adduct. As far as the latter reaction conditions are concerned (use of NaI for the oxyallyl cation preparation) the thiophosphoryl-to-phosphoryl transformation may be explained by the aid of the bromine and/or iodine obtained during the reaction. Indeed, addition of bromine to the solution of **1** in CH_3CN under N_2 atm afforded, among other products the dimer **3**

Table 1. Coupling constants are given in Hz; δ in ppm

	$C_{6,7}$–R	$C_{1,5}$–R'	$C_{2,4}$–H	$C_{2,4}$–R''	P–Ph
R = H R' = Ph R'' = Ph 7	7·03 d $^3J_{PH_{6(7)}}$ = 21	6·7–7·3 m	5·25 d $^3J_{PH_{2(4)}}$ = 7·5	6·7–7·3 m	6·7–7·3 m
R = CH_3 R' = H R'' = CH_3 2	1·75 d $^4J_{P(CH_3)}$ = 2·3	2·65 dd $^2J_{PH}$ = 13·5 $J_{H_{1(4)}H_{2(3)}}$ = 1	3·40 ddqr $^3J_{PH}$ = 7·5 $J_{H_{2(4)}(CH_3)}$ = 7·5 $J_{H_1H_2(H_4H_5)}$ = 1	1·28 dd $^4J_{P(CH_3)}$ = 2·3 $J_{H_{2(4)}(CH_3)}$ = 7·5	7·25–7·75 m
R = CH_3 R' = H R'' = Ph 4	1·58 d $^4J_{P(CH_3)}$ = 1·5	2·99 dd $^2J_{PH}$ = 13·5 $J_{H_1H_2(H_4H_5)}$ = 1·5	4·65 dd $^3J_{PH}$ = 7·5 $J_{H_1H_2(H_4H_5)}$ = 1·5	7·23 s	7·05–7·80 m

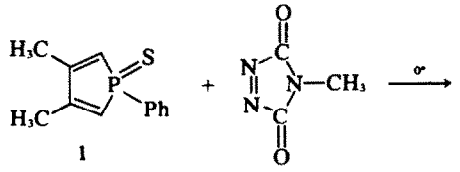
of the phosphole oxide (**8**). The situation was less clear in the case of the Zn(Cu) couple (no reaction occurs when omitting the dibromoketone from the reaction mixture). A possible mechanism for the exchange from a P=S to a P=O group, under these as well as under the former described reaction conditions, will be discussed later.

In order to determine whether a phosphole oxide can possibly undergo the cycloaddition reaction with the oxyallylic cation, the stable 1,2,5-triphenyl phosphole oxide (**6**)[10] (which does not dimerize) was submitted to the reaction conditions (α,α'-dibromodibenzyl ketone, NaI, CH_3CN, N_2, Δ) and indeed an adduct (**7**) was obtained in 90% yield (Table 1 and Experimental). The usefulness of the NMR-shift reagent[11] could once more be seen, in the structure determination of **7**; addition of $Eu(fod)_3$ to a solution of compound **7** (molar ratio of 0·52) in $CDCl_3$ revealed the signal of the $C_{6(7)}$ vinylic protons. (In the absence of the complexant, this signal is hidden among the signal of the five phenyl groups).

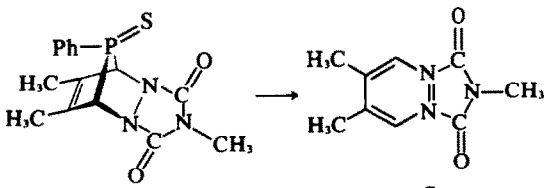
A second phosphole oxide which was examined was the 1-phenyl-3,4-dimethylphosphole oxide[6] (**8**), the corresponding oxide of **1**. Once again an adduct (**4**) with the dibenzyl-allyl cation could be obtained, however only in low yields (~6%), the dimer **3** being the major product (Scheme 1). The last experiment confirmed the possible synthesis of **4** from **8** but does not exclude its origination from **1**; the differences in yields found for the two reactions may result from the preparation of **8** *in situ*, while using the phosphole sulfide, which thus lowers the extent of dimerization.*

The NMR spectrum of the three bicyclic compounds (**2**, **4** and **7**) are compared in Table 1. Most significant in these spectra was the $^3J_{PH_{2(4)}}$ value of 7·5Hz found for all three compounds, indicating the C-2, C-4 protons to be axial (a PC, $CH_{2(4)ax}$ angle of *ca* 60° is in accordance with a 5–7Hz coupling constant, whereas the equatorial proton with an angle of *ca* 170° should exhibit a J-value of *ca* 30Hz).[13]† The fact that only the diequatorial substituted compounds were obtained, was not surprising whether resulting from the preference of the "compact transition state" over the "extended one"[1] or even from a thermodynamic controlled process (if equilibrium can occur under the reaction conditions). The *trans*-2,4 isomer as well as the *cis*-2β,4β one (which is expected to flip over into the boat conformer) are both expected to be less favored, due to strong steric interactions with the phosphoryl group. The $J_{H_1H_2}$ (or $J_{H_4H_5}$) value of 1Hz, is in accordance with a *ca* 75° angle measured for the suggested structure.[14] Indeed, this J-value also agrees with the *ca* 105° angle measured for the *cis*-2β, 4β isomer, however the latter is excluded by the $J_{PCCH_{2(4)}}$-value (an angle of *ca* 130° demands a J-value of more than 20Hz).[13] The P-phenyl configuration was

*In order to find out whether the phosphole sulfide (**1**) is ever capable of entering a Diels–Alder reaction as a diene, its reaction with the excellent dienophile 4-methyl-1,2,4-triazoline-3,5-dione[12] was performed. This reaction is now under further investigation.

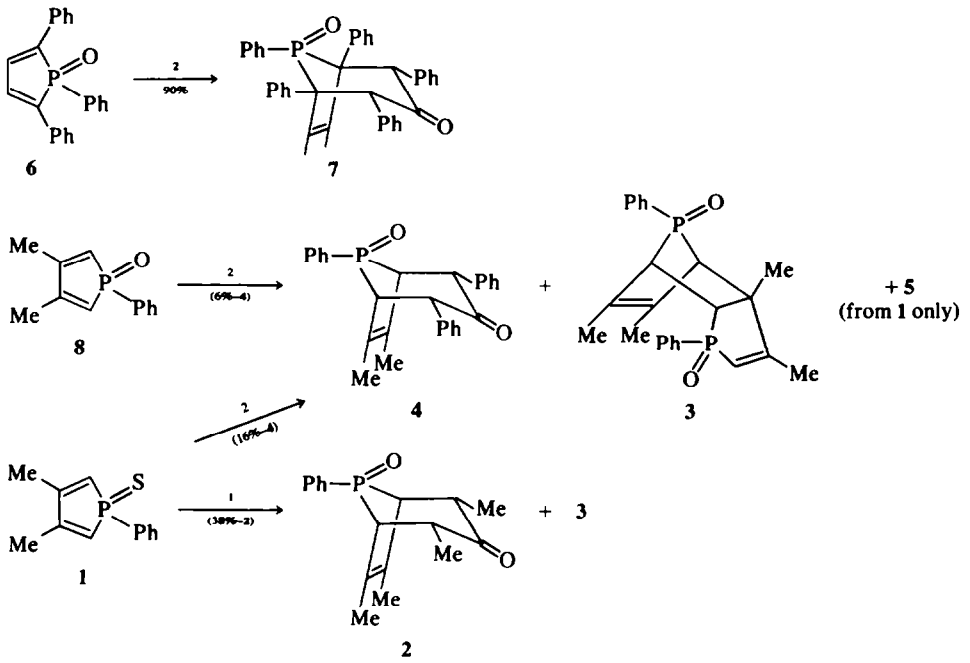


1 **10**



f **g**

†In the case of the 8-methyl-8-oxo-8-phosphabicyclo[3.2.1]oct-6-en-3-one the following values were measured: $^3J_{PH_{2(4)ax}}$ = 6Hz and $^3J_{PH_{2(4)eq}}$ = 27Hz.



1. $CH_3CHBrCOCHBrCH_3 + Zn(Cu), N_2$, glyme. 2. $PhCHBrCOCHBrPh + NaI, N_2, \Delta, CH_2CN$

SCHEME 1.

determined by complexation of the adducts with $Eu(fod)_3$ as has already been described,[3] and it turned out to be the expected equatorial one (towards the phosphorinane ring) in all three compounds.

Although the yields of the 8-phosphabicyclo[3.2.1]octanic systems prepared according to this method are not always high, it can serve as a convenient synthesis for substituted derivatives which can not be readily obtained by the two previously described methods of synthesis.[2,3] The reason for low yields in some cases can be sought in the nature of the diene as well as the experimental conditions:

(a) In the absence of great excess of the diene, which usually also serves as the solvent for these reactions, the reactive oxyallyl cation undergoes undesired side reactions;[1] (b) The high reactivity of the phosphole oxide results in large amounts of the dimer (Outstanding in this respect is **6** which gives much higher yields); (c) Under the reaction conditions even the phosphole sulfide undergoes dimerization, most likely being previously converted to the corresponding oxide *vide infra*.

As mentioned above compounds **3** and **4** were accompanied by another compound (**5**) the yield of which changed remarkably according to the reaction conditions (gradual addition of the dibromodibenzyl ketone to the reaction mixture increased the yield ten fold). The nature and mechanism of obtaining this compound (**5**) follows. Compound **5**, m.p. 202°–204° (dec.), $C_{27}H_{25}O_2SP$ (*m/e* 444 M^+), ν_{max}^{KBr} 3030 (Ph), 1600, 1495, 1440 (Ph–P), 1715 (C=O), 1630 (C=C) 1195 s (P=O) cm^{-1}, exhibits the following NMR spectrum: δ 1·00 d ($^4J_{P-CH_3}$ = 1Hz, 3H), 1·73 d (J_{P-CH_3} = 1Hz, 3H), 3·73 dd (J_{PH} = 7·5Hz, J_{HH} = 1·5Hz, 1H), 4·32 d (A) and 3·58 d (B) (an AB quartet J = 16·5Hz), 4·03 dd (J_{PH} = 7·5Hz and J_{HH} = 1·5Hz, 1H) and 6·75–7·80 m (15H), (Fig 1). The existence of two Me-groups as well as three phenyls indicate that both reactant moieties are indeed included in **5**, however a structure proposal at this stage was impossible. The existence of the phosphoryl group, in addition to the S atom which was still in the molecule was unexpected.

(This is in contrast to the situation with compounds **3** and **4** where the P=S was converted into the P=O with loss of the S-atom). According to the elemental analysis, the molecule was expected to contain, apart from the three phenyls, C=O and P=O sites, three additional unsaturations, i.e. double bonds and/or cyclic rings. However, it was difficult to suggest a structure fulfilling these requirements and at the same time being also in accordance with the NMR data, mainly the requirement for one saturated methyl (δ 1·00) and another vinylic one (δ 1·73). Heating of **5** to 150°–160° in an inert solvent resulted in its decomposing to unidentified sulfur containing compounds. Hydrogenation of **5** under various conditions, i.e. Pd/C, Pt/C or large excess of RaNi, which was supposed to overcome the expected poisoning of the catalyst by the sulfur, or even cause desulfurization of compound **5**, gave unidentified products. In addition submitting of **5** to H_2O_2 or $NaIO_4$ in order to oxidise the S atom, suspected to be part of a thioether moiety, to a sulfone or at least a sulfoxide left it surprisingly unchanged. However this reaction once more confirmed the absence of the P=S in the molecule, which had it been

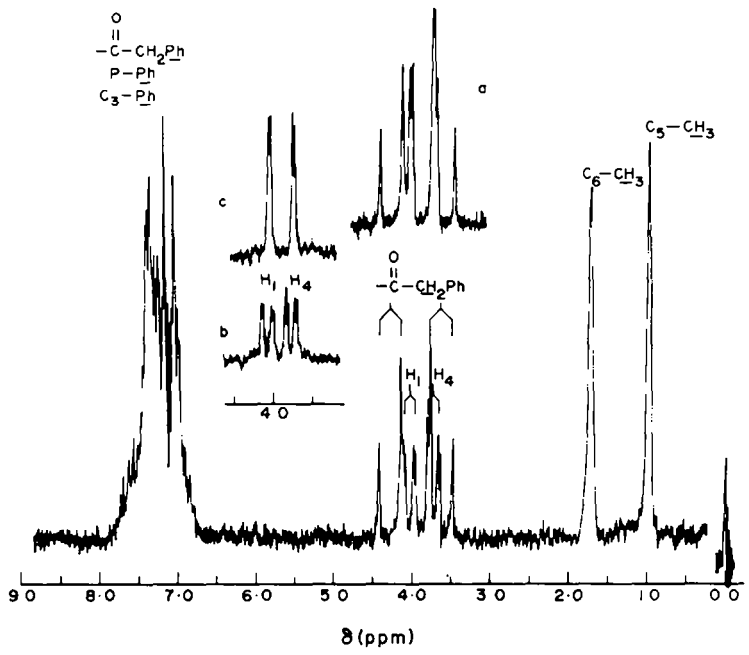
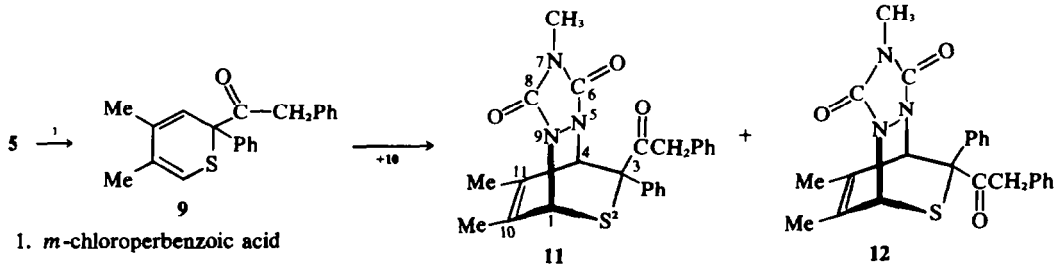


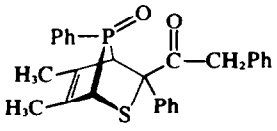
Fig. 1. NMR spectrum of compound **5** (60 MHz). a. phosphorus spin decoupled. b. partail spectrum of compound d_2-**5** and c. phosphorus spin decoupled of the latter signal.

left there should have been converted to a phosphoryl group. The reaction which lead to the break through was the oxidation with m-chloroperbenzoic acid. The peracid was found to attack compound **5** immediately, even at low temperatures, to give a whole series of compounds. However conditions could be found, upon which only one main compound was obtained; adding one equivalent of the peracid to the solution of compound **5** in CH_2Cl_2 at $-10°$, caused immediate coloring of the solution, disappearance of the starting material, and the appearance of mainly one new compound-**9**. Following chromatography, pure **9** (50%) could be obtained; m.p. 97°-98°, $C_{21}H_{20}OS$, (*m/e* 320 M^+), δ ($CDCl_3$) 1·80 d (J = 1·5Hz, 3H), 1·92 d (J = 1·5Hz, 3H) 3·65 s (2H), 5·83 brs (1H), 6·05 brs (1H), 6·95–7·50 m (10H), ν_{max}^{KBr} 3050, 3020, 1600 (Ph), 1710 (C=O) no P=O absorption. All these data indicate that **5** formally lost a PhPO unit, to give, most likely, a diene. Two vinylic protons each being coupled to one out of two vinylmethylic groups, in the NMR spectrum, may suggest the $-CH=C(CH_3)-C(CH_3)=CH-$site. Furthermore the signal at 3·65 s (2H) could be attributed to two benzylic protons ($-COCH_2-Ph$) which most likely belong to the same two protons giving rise to the observed AB quartet (2H, which are not coupled by the P-atom) appearing in the NMR spectrum of **5**. Assuming that no C–C bond migration occurs, the latter signals in **5** and **9**, should point towards the existence of a $PhCC(O)CH_2Ph$ site originating from the oxyallyl cation, which brings us to the suggestion that 1-thia-6-phenyl-6-(1'-keto-2'-phenethyl)cyclohexa-2,4-diene is the structure of **9**. To ascertain the diene moiety in **9**, we choose the Diels–Alder reaction and more particularly the 4-methyl-1,2,4-triazoline-3,5-dione (**10**) as dienophile. Compound **10** is known as an excellent dienophile, reacting even if very strained adducts result.[12b] In the event two 1:1 adducts, between **9** and **10** could be obtained, giving **11** and **12** (Experimental data), thus



SCHEME 2.

confirming the diene structure (Scheme 2). Furthermore, the fact that two adducts were obtained* is in accordance with a suggested chiral center in these compounds, the existence of which may explain the prochiral benzylic protons in **5**, **9**, **11** and **12** (appearing as an AB or A_2-like pattern). The pronounced diastereomerism of the two benzylic protons in **5**, **11** and **12**, in contrast to the situation in **9**, has to be due to large intrinsic diastereomerism as well as non equivalent population of the rotamers around the CO–CH_2Ph bond, both originating from the presence of a heterobridge in **5** (*vide infra*) **11** and **12**. The absence of such a bridge in **9**, which is also responsible for the conformational flexibility of its structure, accounts for the A_2-like pattern (of the benzylic protons) in this case. Of special interest in the NMR spectrum of **11** were the chemical shifts of the two Me groups, one of which appears as high as δ 1·10 while the second appears at δ 1·85, as expected for the vinyl-methylic group. In the second isomer (**12**) both vinyl-methyls appear in the appropriate range (1·88 and 2·00 ppm). This high value (δ 1·10) can be best explained by a diamagnetic effect of the C-3 phenyl group on the spatial neighbour C-11–CH_3 which due to the rigid structure of **11** is sterically oriented as to be strongly influenced. This outstanding value brought us back to the δ 1·00 ppm value found for one of the two Me-groups, believed to be a saturated one, in the NMR spectrum of **5**. On the grounds of the NMR spectrum of **11** we suggest a similar rigid bicyclic system of **5**, namely 2-thia-*endo*-3-phenyl-*exo*-3(1′-keto-2′-phenethyl)-5,6-dimethyl-7-phenyl-7-oxo-7-phosphabicyclo[2.2.1]hept-5-ene.



5

Such a compound is expected to be even more rigid than **11** and **12**, which thus explains the relatively high field position of the C_5-Me-vinyl group signal. Furthermore the 1·5 Hz coupling constant between C-1-H and C-4-H can be explained by a long range coupling known to exist in such bicyclo[2.2.1] compounds.[16] Compound **9** is therefore obtained from **5** by a formal elimination of a PhPO group as a result of the *m*-chloroperbenzoic acid oxidation.

Indeed thermal PhPO extrusion from strain compounds like 7-phenyl-7-oxo-7-phosphabicyclo[2.2.1]hepta-2,5-dienes,[5]† is known at 155°[17]; however in these cases the

*No *exo-endo* isomerization is expected for the triazoline adducts. As in the case of 1,2-succinoyl-4,5-dimethyl-1,2,3,6-tetrahydropyridazine,[15] a low inversion barrier for the nitrogens is expected, and indeed cooling down the NMR sample of **11** to −120° caused significant broadening of the N-Me line with respect to the other two methyls. Furthermore, an *exo-endo* isomerization is excluded by the NMR data, i.e. if this were the case both C-methyl groups of **11** and **12** would be expected to be similarly shifted.

†The 7-phosphabicyclo[2.2.1]heptene is also known to lose the PhPO but at higher temperatures[5]—it may be that this process occurs also by heating of **5**.

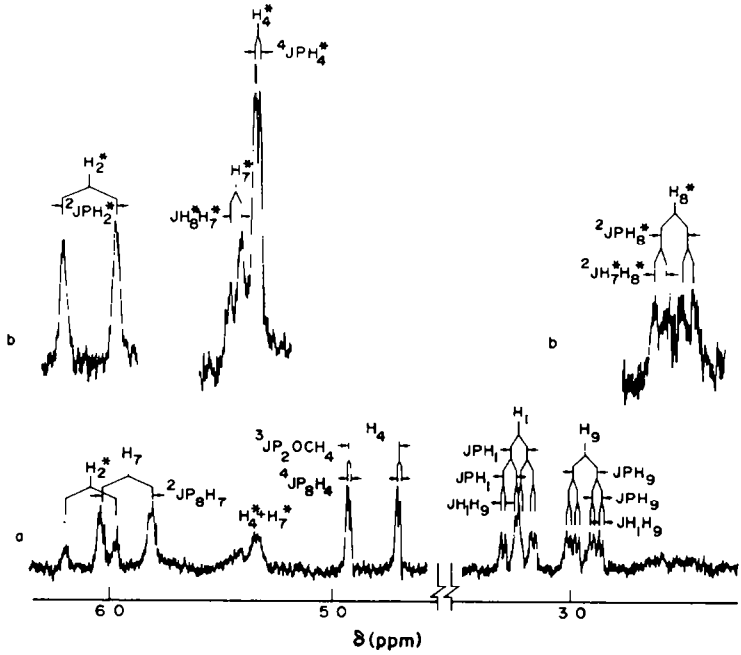
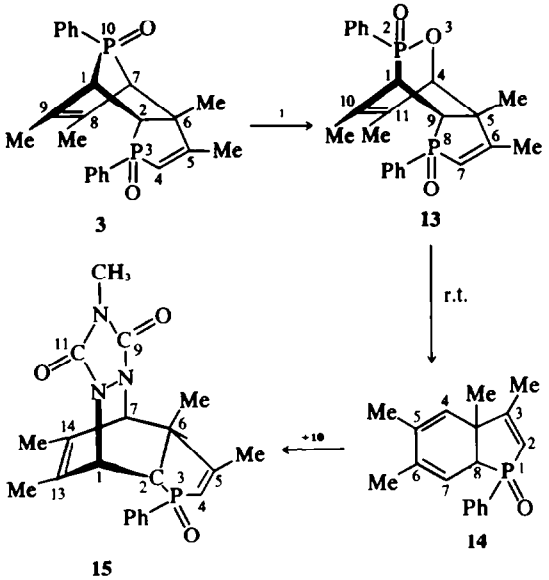


Fig. 2. Partial NMR spectrum of compounds **13** and **14** (100 MHz). *Signals of compound **14**. a. spectrum of compound **13**, containing about 20 per cent of **14**. b. spectrum of pure **14**.

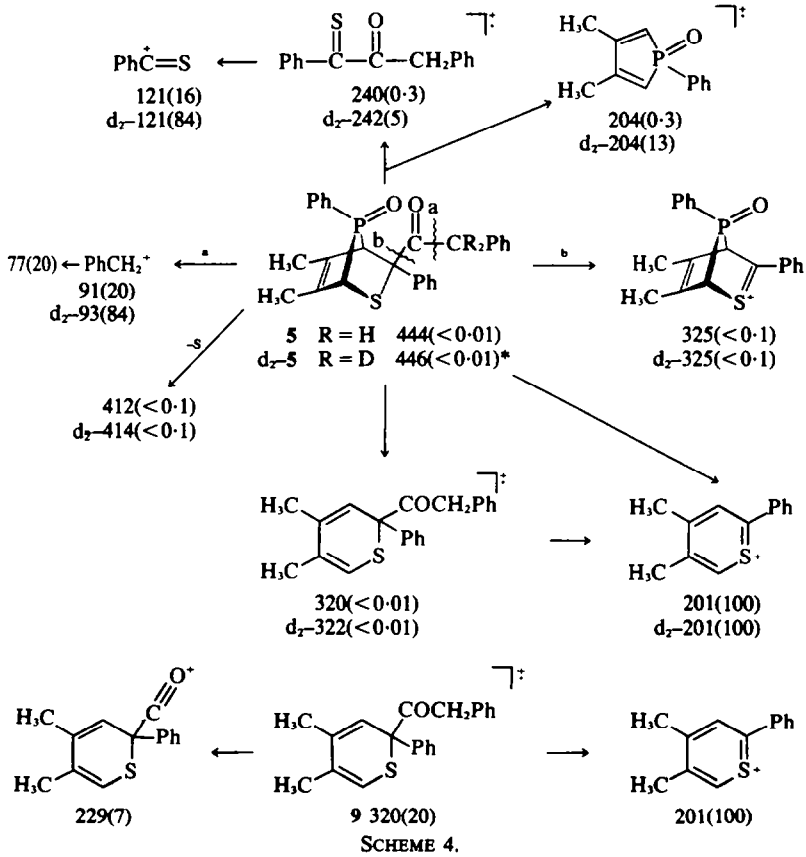


SCHEME 3.

1. *m*-chloroperbenzoic acid

cleavage occurs without any oxidant, the driving force being the aromatization energy which is gained. For the purpose of examining the generality of the oxidative extrusion, another strained compound containing the 7-phosphabicyclo[2.2.1]heptenic system which is not expected to undergo aromatization by removal of the PhPO unit, was undertaken. A model which fits the above demands is the dimer of 3,4-dimethylphosphole oxide (**3**). (The conjugated double bond C_4C_5 in **3** is known to undergo epoxidation with the *m*-chloroperbenzoic acid only under drastic conditions).[18] Addition of the peracid to a solution of **3** in $CHCl_3$ resulted in almost immediate conversion to a new unstable compound **13**. After *ca* 15 min at r.t. another compound (**14**), resulting from compound **13**, could be seen on a TLC plate. The conversion of compound **13** to **14** could be followed by the NMR spectrum of purified **13** (*ca* 80% pure), (Fig 2), obtained from a chromatography column.

Compound **14** m.p. 153°–154°; $C_{18}H_{21}O$ P(*m/e* 284 M^+), δ 1·20 s (C_5–CH_3); 1·85 m (C_5–CH_3 and C_6–CH_3); 2·10 m (C_3–CH_3); 2·55 ddm ($^2J_{PH_8}$ = 12Hz; $J_{H_7H_8}$ = 5Hz; H_8); 5·35 d ($^4J_{PH_4}$ = 2Hz; H_4) 5·45 dm ($J_{H_8H_7}$ = 5Hz, H_7); 6·10 dm ($^2J_{PH_7}$ = 24Hz, H_2); 7·3–7·9 m (Ph, 5H), is indeed a diene, namely 1-phenyl-1-oxo-3,5,6,9-tetramethyl-8-



SCHEME 4.

Mass spectra of compounds **5** and **9**.

*The strong variation in the intensity of the peaks of **5** in comparison to d_7–**5** are most probably due to variations in the inlet temp.

hydrophosphindole, and as such could give an adduct (**15**) with the triazoline (**10**) (Scheme 3). As mentioned in a previous report,[4] compounds like **3** are expected to react with the peracid to undergo Bayer-Villiger-like oxidation, thus compound **13** should be a phosphinate. Being unstable, compound **13** could be characterized only by its NMR spectrum (Fig 2 and Experimental). In the mass spectrum it is converted to **14**; i.e. the highest *m/e* value was 284 which fits in the molecular ion of **14**.

The most striking feature in the NMR spectrum was the signal at 4·84 dd ($^3J_{P,OCH_4}$ = 22Hz; $^4J_{P,H_4}$ = 2Hz; H_4; Fig 2) atrributed to the proton α- to the phosphinate-bearing C-atom, appearing in **3** at 3·3 m. Similar values for such protons were found in the case of the phosphinates obtained from the 8-phosphabicyclo[3.2.1]octenic system.[4] The latter bicyclo[3.2.2] systems, being less strained, do not undergo the $PhPO_2$ extrusion, but epoxidation which thus stabilizes the compounds. As far as we know this $PhPO_2$ elimination, which leads to **14** from **13** is unknown. It is suggested that compound **5** should be converted to **9** by a similar intermediate, which being more strained could not be isolated.

The elimination of $PhPO_2$ is by itself very interesting, furthermore compounds of type **13** may serve as $PhPO_2$ suppliers for synthetic use.* In the absence of compounds that may react with the $PhPO_2$ molecule it is suspected to undergo oligomerization as in the case of metaphosphoric acid,[19] or the PhPO group.[17]

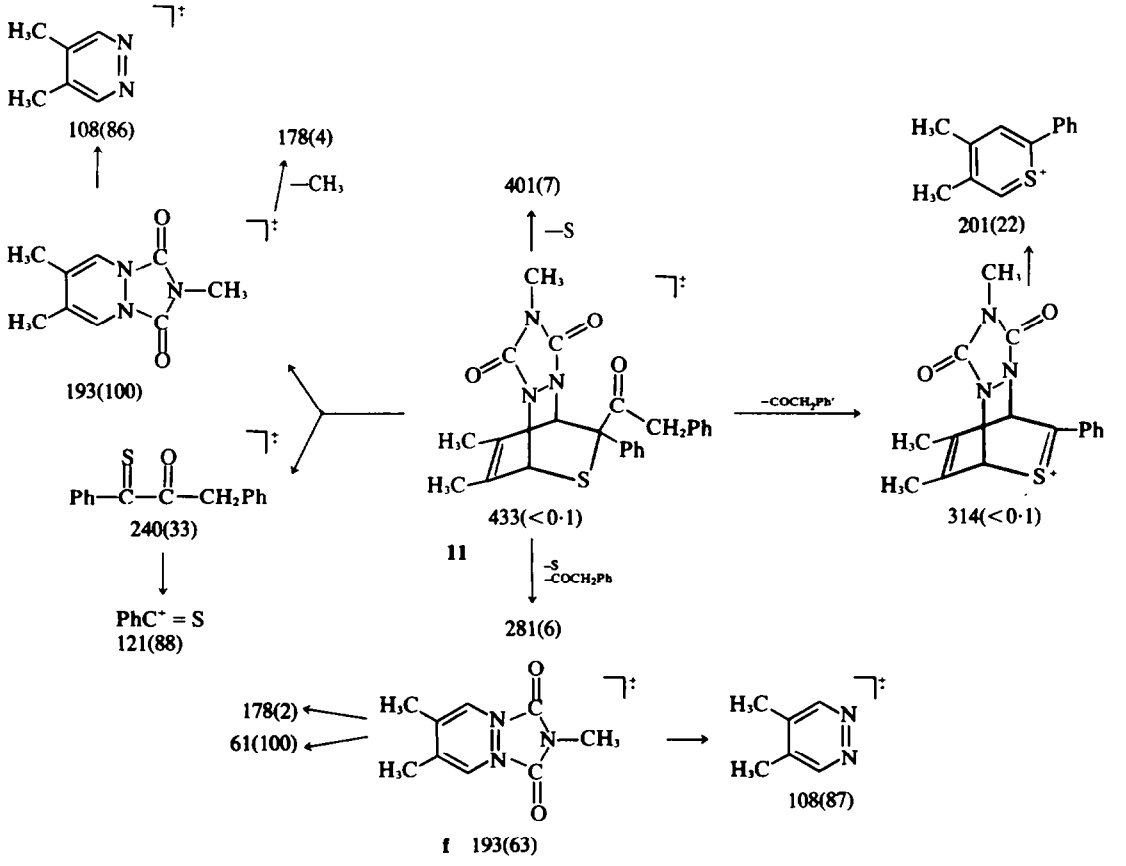
The mass spectra of compounds **5**, **9**, **11**, **12** and **f** shown in Schemes 4 and 5, are in full agreement with the proposed structures.†

The following mechanism (Scheme 6) is suggested for the reaction leading to compound **5**.

The first step is expected to be the oxyallyl cation attack on the P=S bond, rather than the diene, to give a phosphole spirane **k**. Phosphole spianes are known, and in one particular case such a pentacovalent compound could even be isolated at r.t.[20] Furthermore 1-oxo-3-

*Following CH_2N_2 addition to the solution of **13** in ether–methanol (9:1), phenyldimethyl phosphonate was isolated; an oil, ν_{max}^{neat} 3030, 2940, 2830, 1590, 1460, 1240, 1170, 1120, 1045, 1020, 960 cm^{-1}; δ 3·78 d (J_{POCH_3} = 11Hz; $POCH_3$; 6H) and 7·3–8·0 m (Ph); *m/e* (%): 186 (61), 185 (61), 172 (23), 171 (19), 156 (35), 155 (37), 142 (16), 141 (51), 91 (100), 77 (77).

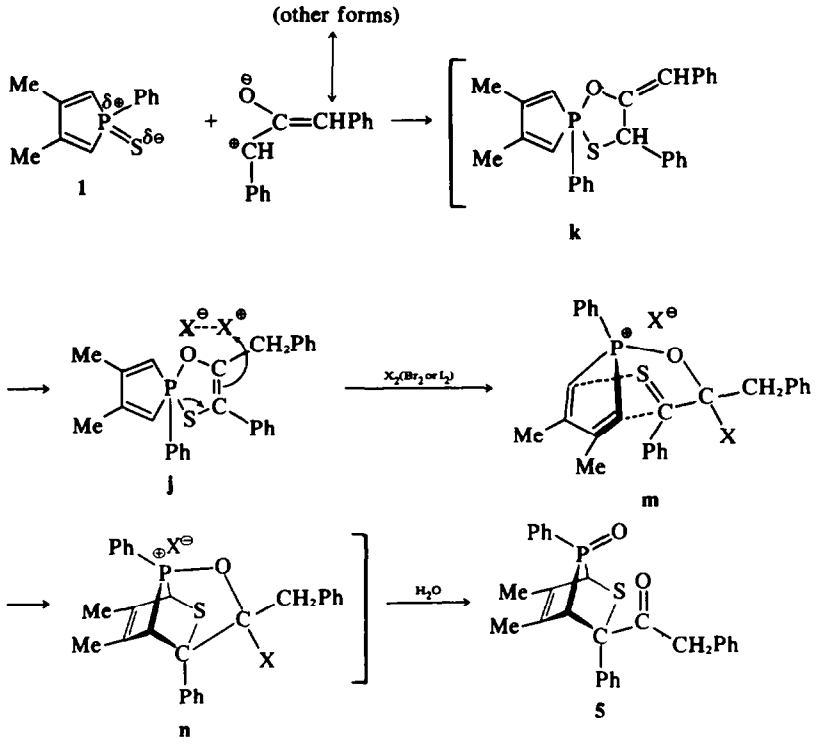
†For this purpose as well as for further NMR study (Fig 1), the d_2-**5** compound was prepared (Experimental).



SCHEME 5.*

Mass spectra of compounds 11 and f.

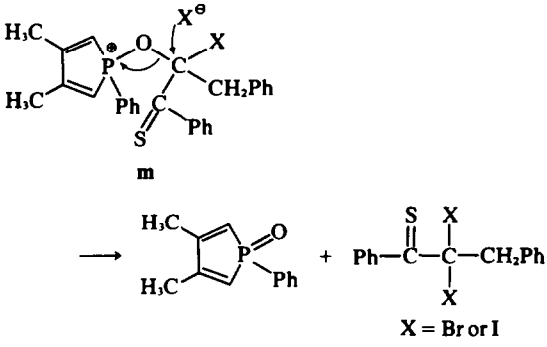
*The mass spectra of **12** is undistinguishable from that of **11**.



SCHEME 6.

thiophospholane has been suggested as an intermediate in the conversion of oxiranes to thiiranes.[21] The step after tautomerization of **k** to **j**, can be pictured as an electrophilic attack by bromine or iodine on the phosphorane **j** leading to intermediate **m**. The mechanism of phosphorane opening by bromine, already investigated by Ramirez[22] in the case of the 2,2,2-trioxy-2,2-dihydro-1,3,2-dioxaphospholenic ring, supports the possibility of a similar path way in our case. Intermediate **m** is then believed to undergo a very preferential intramolecular Diels–Alder reaction between the reactive thiocarbonyl dienophile[23]* and the phospholium salt (**m**) as a diene.† Once the tricyclic system (**n**) is obtained, it should undergo rapid hydrolysis upon work up, in order to release the strain and to provide a more stable structure; thus leading to the 2-thia-7-phosphabicyclo[2.2.1] system (**5**). The proposed mechanism is in agreement with the suggested P=O and C-3 configuration i.e. the $COCH_2Ph$ group being spatially near the P=O one.

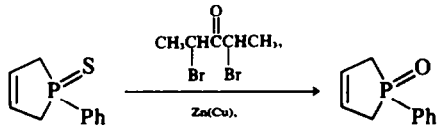
Once the thiophosphoryl attack by the oxyallyl cation leading to the oxa-thiaphosphorane (**j**) is expected, intermediate **m** may decompose competitively to the Diels–Alder reaction, by substitution of a halide ion at the position α to the C=S group.[22]



This sequence leads to the phosphole oxide which, as described above, will lead to compounds **2** and **3**. The oxa-thiaphosphorane (**j**) can obviously also be suggested in the case when the oxyallyl cation is prepared by the use of the Zn(Cu) couple. However under these reaction conditions compound **5** is not obtained. Moreover, as no halogen is expected to be present in the reaction mixture[1] some other factor should be responsible for the decomposition of **j** to the phosphole oxide. Indeed, submitting 3-phospholene sulfide (**16**) to these reaction conditions converted it almost quantitatively to the corresponding oxide (**17**).

*The C=S bond in **m** is expected to be even more activated by the two-electron attracting groups.[23]

†A positive charge on the P-atom is expected to improve this diene as can be seen by the comparison of phosphole oxide and the phosphole sulfide; the former P-atom being more positive charged.



16 17

Further investigation of the various factors in the decomposition of the phosphorane (**j**) into the phosphole oxide, may be obtained if the phosphole sulfide **1** would be reacted with dimethyl cyclopropanone,[24] under various reaction conditions. This may enable the examination of the oxa-thiaphosphorane stability; attempts in this direction are undertaken.

EXPERIMENTAL

For general directions see Ref 3.

Starting materials. 1,2,5-Triphenylphosphole and its oxide (**6**) were prepared according to the method of Hughes *et al.*;[5] 3,4-dimethyl-1-phenylphosphole, the sulphide (**1**) and the dimer (**3**) of the oxide analog, were synthesized using the method of Mathey.[6] 3,4-Dibromo-3,4-dimethyl-1-phenyl phospholan-1-oxide was prepared according to Quin's method;[25] α,α'-dibromodibenzyl ketone was synthesized in a method described by Breslow *et al.*;[26] 2,4-dibromo-3-pentanone was prepared according to Doerer *et al.*[27]

2,4,6,7-*Tetramethyl*-8-*phenyl*-8-*oxo*-8-*phosphabicyclo*[3.2.1]*oct*-6-*en*-3-*one* (**2**). 2,4-Dibromo-3-pentanone (freshly distilled, 2·5 g) was added dropwise to a cooled (−10°), stirred soln of **1** (2 g) in dry glyme (35 ml) in the presence of freshly prepared Zn(Cu) (0·5 g) under N_2. Another portion of Zn(Cu) (0·5 g) was added within every 1/2 h (4 portions). This whole procedure was repeated 4 times, the last two being carried out under heating (80°). (The total amounts added were: 10 g of dibromoketone and 10 g of Zn(Cu)). The metal was then filtered and the soln diluted ($CHCl_3$, 300 ml) washed with water, 1N HCl aq (50 ml) and again water, dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The viscous, yellow oily product (4·8 g) was chromatographed on a silica column. The product **2**, eluted with MeOH–EtOAc (V/V 5:95) (0·99 g), was followed by the dimer **3** (1·39 g). Compound **2** m.p. 156°–157° (ether); ν_{max}^{KBr}: 3020, 2900–2850, 1720, 1475, 1445, 1390, 1350, 1200, 1170, 1130, 1110, 1080, 1030, 995, 920, 850, 815, 750, 700, 550, 495, 460 cm^{-1}. δ 1·28 dd ($J_{C_3(4)H-CH_3}$ = 7·5Hz; $^4J_{P-CH_3}$ = 2·3Hz; $C_2(CH_3)$, $C_4(CH_3)$; 6H); 1·75 d ($^4J_{P-CH_3}$ = 2·3Hz; $C_6(CH_3)$, $C_7(CH_3)$; 6H); 2·65 dd ($^2J_{PH_{1(5)}}$ = 13·5Hz; $J_{H_1H_2} = J_{H_4H_5}$ = 1Hz; H_1, H_5; 2H); 3·40 dd quartet ($^3J_{PH_{2(4)}}$ = 7·5Hz; $J_{H_1H_2} = J_{H_5H_4}$ = 1Hz; H_2, H_4; 2H); 7·25–7·75 m (Ph–H; 5H) ppm. (Found: M^+ 288; $C_{17}H_{21}O_2P$ requires: MW 288).

2,4,8-*Triphenyl*-6,7-*dimethyl*-8-*oxo*-8-*phosphabicyclo*[3.2.1]*oct*-6-*en*-3-*one* (**4**). 1,5-Diazabicyclo[5.4.0]undec-5-ene (DBU; 6·3 g) was rapidly added to a cooled, stirred soln of 3,4-dibromo-3,4-dimethyl-1-phenylphospholan-1-oxide (7·5 g) in dry benzene (50 ml) under N_2 (1 h). The brownish ppt was filtered off and the soln washed twice with 1N HCl aq (2 × 15 ml), water, dried (Na_2SO_4) and most of the solvent evaporated under reduced pressure (minimal heating) yielding a reddish, oily product containing white, crystalline solid. The crystals (dimer **3**; 1·5 g) were filtered off and the residual soln was diluted with dry CH_3CN (50 ml) to which NaI (7·5 g) and α,α'-dibromodibenzylketone (2·5 g) were added. The mixture was then refluxed under N_2 (3 h). After cooling, the mixture was diluted in $CHCl_3$ (150 ml), washed with 10% $Na_2S_2O_3$-aq (2 × 15 ml), then water, dried (Na_2SO_4) and evaporated to dryness. The dark, oily product (3·76 g) was chromatographed on a silica column. Product **4** was eluted with benzene-EtOAc (V/V 1:1) (0·5 g, 6%) followed by dimer **3** (1·3 g). Compound **4** m.p. 202°–204° (EtOH, dec), ν_{max}^{KBr}: 3050, 3030, 3000, 2950–2830, 1705, 1600, 1595, 1500, 1455, 1445, 1390, 1215, 1190, 1135, 1110, 1090, 1025, 995, 850, 800, 765, 750, 710, 700, 560, 535, 510, 490, 455 cm^{-1}, δ 1·58 d ($^4J_{PCH_3}$ = 1·5Hz; $C_6(CH_3)$, $C_7(CH_3)$; 6H); 2·99 dd ($^2J_{PH_{1(5)}}$ = 13·5Hz; $J_{H_1H_2} = J_{H_4H_5}$ = 1·5Hz; H_1, H_5; 2H); 4·65 dd ($^3J_{PH_{2(4)}}$ = 7·5Hz; $J_{H_1H_2} = J_{H_5H_4}$ = 1·5Hz; H_2, H_4; 2H); 7·23 s (C_2(Ph), C_4(Ph); 10H); 7·05–7·80 m (P(Ph); 5H) ppm. (Found: C, 78·58; H, 6·15; P, 7·39; $C_{27}H_{25}O_2P$ requires: C, 78·62; H, 6·11; P, 7·51%).

2 - *Thia* - endo - 3 - *phenyl* - exo(1' - *keto* - 2' - *phenethyl*) - 5,6 - *dimethyl* - 7 - *phenyl* - 7 - *oxo* - 7 - *phosphabicyclo*[2.2.1]*hept* - 5 - *ene* (**5**). α,α'-Dibromodibenzylketone (2 g) and NaI (3·5 g) were added to a stirred soln of **1** (6·60 g) in dry CH_3CN(75 ml). The mixture was refluxed under N_2 (1 h). Another portion of the dibromo ketone (2·0 g) and NaI (3·5 g) was added, and the reflux continued. This whole procedure was repeated 8 times (the total amounts added were: 20 g of dibromoketone and 35 g of NaI).* After a further reflux period (15 h) the soln was cooled, $CHCl_3$ was added (750 ml) and the reddish soln was washed with 10% $Na_2S_2O_3$ aq (2 × 50 ml), water, dried (Na_2SO_4) and the solvent removed under reduced pressure. The dark-red oily product (17 g) was chromatographed on a silica column. Compound **5** was eluted with benzene-EtOAc (V/V 4:1) (4·05 g 31%) followed by **4** (0·4 g) and the dimer **3** (0·5 g). Compound **5** m.p. 202°–204° (EtOH), ν_{max}^{KBR}: 3030, 3000, 2900–2825, 1715, 1630, 1600, 1495, 1445, 1400, 1375, 1320, 1195, 1110, 1085, 1025, 1000, 965, 910, 840, 805, 790, 770, 750, 740, 720, 710, 690, 580, 545, 535, 505, 480, 440 cm^{-1}, δ 1·00 d ($^4J_{P-CH_3}$ = 1Hz; $C_5(CH_3)$; 3H); 1·73 d ($^4J_{P-CH_3}$ = 1Hz; $C_6(CH_3)$; 3H); 3·73 dd ($^2J_{PH_4}$ = 7·5Hz; $J_{H_1H_4}$ = 1·5Hz; H_4; 1H); AB quartet (δ_A = 4·32; δ_B = 3·58; J_{AB} = 16·5Hz; C(O)CH_2Ph; 2H); 4·03 dd ($^2J_{PH_1}$ = 7·5Hz; $J_{H_4H_1}$ = 1·5Hz; H_1; 1H); 6·75–7·80 m (aromatic protons; 15H) ppm. (Found: C, 72·50; H, 5·56; P, 7·25; S, 7·21; $C_{27}H_{25}O_2SP$ requires: C, 72·95; H, 5·67; P, 6·97; S, 7·38%).

Deuteration of compound **5** *to give* d_2-**5**. A soln of **5** (100 mg) in dry dioxane (10 ml) and fresh D_2O (2 ml) was heated (85°, 15 h) under N_2 in the presence of a catalytic quantity of anhyd K_2CO_3. The solvents were evaporated to dryness, the residue dissolved in $CHCl_3$ (50 ml), washed with D_2O (5 ml), dried (Na_2SO_4) and evaporated, yielding a white solid. m.p. 201°–202° (EtOH, dec); ν_{max}^{KBr}; 2200 (C-D) cm^{-1}. The NMR spectrum showed the disappearance of the AB quartet appearing in the spectrum of **5** (δ_A = 4·32; δ_B = 3·58; J_{AB} = 16·5 Hz; –$COCH_2$Ph; 2H).

1,2,4,5,8 - *Pentaphenyl* - 8 - *oxo* - 8 - *phosphabicyclo*[3.2.1]*oct* - 6 - *en* - 3 - *one* (**7**). Compound **6** (1·68 g) was reacted with α,α'-dibromo dibenzylketone (10 g) in the presence of NaI (20 g) in CH_3CN–$CHCl_3$ (60 ml; V/V 5:1) under N_2, according to the procedure described for **5**. Compound **7** precipitated as a white solid, after reducing the volume of the $CHCl_3$soln to 50 ml (2·50 g, 91%). m.p. 286° ($CHCl_3$-toluene, dec) ν_{max}^{KBr}: 3050, 3020, 3000, 2930, 1710, 1600, 1495, 1445, 1435, 1180, 1110, 1070, 1030, 990, 940, 810, 740, 690, 600, 535, 520 cm^{-1}, δ 5·25 d ($^3J_{PH_{2(4)}}$ = 7·5 Hz; H_2, H_4; 2H); 7·03 d ($^3J_{PH_{6(7)}}$ = 21 Hz; H_6, H_7); 6·70–7·30 m (aromatic protons) (27H) ppm. (Found: C, 82·58; H, 5·36; P, 5·73; $C_{37}H_{29}O_2P$ requires: C, 82·79; H, 5·45; P, 5·77%).

1 - *Thia* - 6 - *phenyl* - 6 - (1' - *keto* - 2' - *phenethyl*) - 3,4 - *dimethylcyclohexa* - 2,4 - *diene* (**9**). *m*-Chloroperbenzoic acid (80%, 242 mg) was added in small portions to a cooled (−10°), stirred soln of **5** (526 mg) in CH_2Cl_2 (10 ml). The yellowish soln was rapidly chromatographed on neutral alumina column (Merck, grade III; $CHCl_3$). The desired product was eluted as a white solid (273 mg). Recrystallization from MeOH gave white needles (179 mg, 47%). M.p. 97°–98°, ν_{max}^{KBr}: 3050, 3020, 3000, 2940, 2920, 2880, 2830, 1710, 1600, 1590, 1540, 1380, 1340, 1280, 1260, 1200, 1115,

*Compounds **4**, **5** and **3** were obtained (1·0, 0·2 and 1·7 g respectively) when the dibromoketone and NaI were added in two portions only (2 × 5·5 and 2 × 12 g respectively) under the same conditions.

1090, 1065, 1030, 1000, 920, 875, 845, 820, 795, 765, 740, 720, 700, 640, 620, 585 cm^{-1}, δ 1·80 d ($^4J_{H_5CH_3}$ = 1·5 Hz; $C_4(CH_3)$; 3H); 1·92 d ($^4J_{H_5CH_3}$ = 1·5 Hz; $C_3(CH_3)$; 3H); 3·65 s ($-C(O)C\underline{H}_2Ph$; 2H); 5·83 m (H_5; 1H); 6·05 m (H_2; 1H); 6·95–7·30 (C_6(Ph); 5H); 7·47 s ($C(O)CH_2P\underline{h}$; 5H) ppm. (Found: C, 78·06; H, 6·21; O, 5·03; S, 10·24; $C_{21}H_{20}OS$ requires: C, 78·74; H, 6·29; O, 4·99, S, 10·01%).

The reaction between compound **9** *and 4-methyl-1,2,4-triazolin-3,5-dione* (**10**) *to give the adducts* **11** *and* **12**. A soln of **10** (200 mg) in CH_2Cl_2 (2 ml) was rapidly added to a cooled (0°), stirred soln of **9** (147 mg) in CH_2Cl_2 (10 ml). The mixture was stirred for 1 h (0°), the solvent reduced and the residue chromatographed on a neutral alumina column (Merck, grade III; CH_2Cl_2), yielding **12** (70 mg) followed by **11** (118 mg) as white, crystalline solids. Each one was recrystallized from benzene-hexane. Compound **12**, m.p. 164·5°–165·5° (dec), ν_{max}^{KBr}: 3030, 3000, 2950, 2925, 2880, 2830, 1780, 1760, 1740, 1600, 1450, 1400, 1310, 1265, 1185, 1130, 1030, 920, 810, 785, 750, 730, 700, 640, 580, 545, 500 cm^{-1}, δ 1·88 m; 2·02 m ($C_{11}(CH_3)$, $C_{10}(CH_3)$; 6H); 2·88 s ($N(CH_3)$; 3H); AB quartet (δ_A = 3·31; δ_B = 3·58; J_{AB} = 16 Hz; $C(O)C\underline{H}_2Ph$; 2H); 5·37 s (H_4; 1H); 5·48 s (H_1; 1H); 6·70–7·80 m (aromatic protons; 10H) ppm. (Found: C, 66·35; H, 5·48; N, 9·78; S, 7·32; $C_{24}H_{23}O_3N_3S$ requires: C, 66·48; H, 5·35; N, 9·69; S, 7·39%). Compound **11**, m.p. 152°–153°, ν_{max}^{KBr}: 3030, 3000, 2910, 2880, 2820, 1775, 1760, 1705, 1600, 1445, 1395, 1330, 1260, 1215, 1195, 1140, 1110, 1030, 920, 780, 760, 715, 700, 670, 640, 620, 590, 540, 525, 485 cm^{-1}, δ 1·09 m ($C_{11}(C\underline{H}_3)$; 3H); 1·85 m ($C_{10}(C\underline{H}_3)$; 3H); 2·80 s ($N(CH_3)$; 3H); AB quartet (δ_A = 3·50; δ_B = 3·84; J_{AB} = 16Hz; $C(O)C\underline{H}_2Ph$; 2H); 5·53 m (H_1, H_4; 2H); 6·70–7·60 m (aromatic protons; 10H) ppm. (Found: C, 66·43; H, 5·28; N, 9·79; S, 7·23; $C_{24}H_{23}O_3N_3S$ requires: C, 66·48; H, 5·35; N, 9·69; S, 7·39%).

The reaction of compound **3** *with m-chloroperbenzoic acid, to give compound* **13**. *m*-Chloroperbenzoic acid (80%, 265 mg) was added in one portion to a stirred soln of **3** (0·5 g) in $CHCl_3$ (15 ml) at r.t. The solvent was then reduced under vacuum (without heating) and the mixture was rapidly chromatographed on a neutral alumina column (Merck, grade III; $CHCl_3$). Compound **13** was eluted as a clear, viscous oil (89 mg) followed by traces of **14** and unreacted **3** (404 mg), δ 1·59 m ($^4J_{PC\underline{H}_3}$ = 2 Hz; $C_5(CH_3)$; 3H); 1·83 m; 1·89 m ($C_{10}(CH_3)$, $C_{11}(CH_3)$; 6H); 2·08 m ($C_6(CH_3)$; 3H); 2·96 ddd (J_{PH_9} = 11Hz; J_{PH_9} = 4Hz; $J_{H_1H_9}$ = 2Hz; H_9; 1H); 3·25 ddd (J_{PH_1} = 7Hz; J_{PH_1} = 4Hz; $J_{H_9H_1}$ = 2Hz; H_1; 1H); 4·84 dd ($J_{P_{(2)}OCH_4}$ = 22Hz; $^4J_{P_{(8)}H_4}$ = 2Hz; H_4; 1H); 5·93 dd ($^2J_{P_{(8)}H_7}$ = 23 Hz; $^4J_{H_7(CH_3)}$ = 1·5 Hz; H_7; 1H); 7·35–80 m (aromatic protons; 10H) ppm.

Compound **14** *from* **13**. Compound **13** (100 mg) in $CHCl_3$ (0·5 ml) was kept at r.t. for 4 h, then chromatographed on a short alumina column ($CHCl_3$), yielding clear, viscous oil (58 mg), m.p. 153°–154° (EtOAc-ether), ν_{max}^{KBr}: 3010, 3000, 2980, 2915, 2885, 2865, 1600, 1590, 1480, 1470, 1390, 1280, 1230, 1190, 1160, 1120, 1100, 1080, 1060, 1030, 1010, 990, 870, 835, 815, 800, 760, 730, 720, 700, 620, 600, 550, 530, 500 cm^{-1}, δ 1·20 s ($C_9(CH_3)$; 3H); 1·85 m ($C_5(CH_3)$, $C_6(CH_3)$; 6H); 2·10 m ($C_2(CH_3)$; 3H); 2·55 ddm ($^2J_{PH_8}$ = 12 Hz; $J_{H_7H_8}$ = 5 Hz; H_8; 1H); 5·35 brd ($^4J_{PH_4}$ = 2Hz; H_4; 1H); 5·45 dm ($J_{H_8H_7}$ = 5Hz; H_7; 1H); 6·10 dm ($^2J_{PH_3}$ = 24Hz; H_3; 1H); 7·30–7·90 m (aromatic protons; 5H) ppm. (Found: M^+ 284; $C_{18}H_{21}OP$ requires: MW 284).

The reaction between compounds **14** *and* **10** *to give compound* **15**. A soln of **10** (0·5 g) in CH_2Cl_2 (5 ml) was added to a cooled (0°), stirred soln of a mixture (containing **13**, **14** and unreacted **3**; 1·25 g) in CH_2Cl_2 (50 ml). Stirring was continued for 15 h (4°). The solvent was reduced to a minimal volume and chromatographed on a neutral alumina column (Merck, grade III; $CHCl_3$) yielding pure **15** (184 mg) and a mixture of **15** and **3** (1·30 gr), m.p. 252°–253° (EtOH–EtOAc) ν_{max}^{KBr}: 3020, 2940, 2900, 2870, 1775, 1760, 1600, 1450, 1400, 1270, 1190, 1155, 1130, 1110, 1070, 1030, 920, 880, 870, 860, 790, 775, 750, 720, 700, 635, 620, 570, 545, 515, 480 cm^{-1}, δ 1·03 s ($C_6(CH_3)$; 3H); 1·78 m; 1·98 m ($C_{14}(CH_3)$, $C_{13}(CH_3)$; 6H); 2·06 m ($C_4(CH_3)$; 3H); 2·38 dd ($^2J_{PH_2}$ = 4Hz; $J_{H_1H_2}$ = 3Hz; H_2; 1H); 3·03 s ($N_{10}(CH_3)$; 3H); 4·65 d ($^4J_{PH_7}$ = 1·5Hz; H_7; 1H); 4·95 dd ($^3J_{PH_1}$ = 3Hz; $J_{H_2H_1}$ = 3Hz; H_1; 1H); 6·92 dm ($^2J_{PH_4}$ = 24Hz; H_4; 1H); 7·40–7·90 m (aromatic protons; 5H) ppm. (Found: M^+ 397; $C_{21}H_{24}O_3N_3P$ requires: MW 397).

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