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CYCLOADDITIONS OF 3,4-DIMETHYL-1-THIO-1-PHENYL PHOSPHOLE

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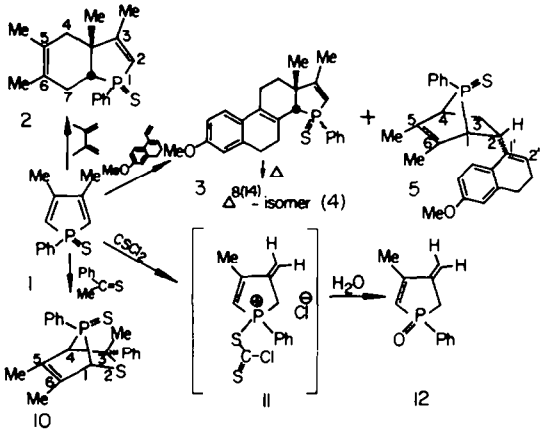
Abstract—Phosphole sulfide **1** undergoes cycloaddition to give a new 15-phosphasteroid. The ^{13}C-NMR and $^{2}J_{PC}$-coupling constants of several compounds prepared similarly are discussed, permitting structure assignment to one of the 7-phosphabicyclo[2.2.1]heptane adducts **5**. Thiophosgene reacts with the P=S moiety of **1**, giving **12** after hydrolysis, through a P=S to P=O transformation coupled in case of **1** with a proton migration.

The reactivity of phospholes, coupled with our interest in phospha-polycycles and steroids, prompted us to examine cycloaddition reactions of phosphole sulfides with several olefinic compounds.[1,2] Phospholes are poor dienes, though the oxides, e.g. 1-phenyl-1-oxo-3,4-dimethyl phosphole **1**[3] are at least as good as cyclopentadiene and undergo rapid dimerization.[4] In contrast to the oxide the phosphole sulfide does not undergo dimerization and has already been used by us in cycloaddition reactions with tropone and oxyallyl cations.[1,2] Whereas compound **1** undergoes the reaction with the reactive two electron system (oxyallyl cation) as a diene, it reacts with tropone as a dienophile.

We wish to describe further the chemical behavior of **1**, namely its reaction with several dienes and dienophiles, leading to, among other new compounds, a new phosphasteroid.

The reaction of **1** with the reactive 2,3-dimethyl butadiene was the first one to be tested; only traces of an adduct could be found after heating both reactants under reflux, in benzene solution, for 1 week. After 12 hr at 140° in a sealed tube a 1:1 adduct, isolated upon repeated chromatographies, was obtained; an oil, $C_{18}H_{23}PS$; *m/e* 302 (M^+, 100%).

The tetrahydrophosphindole structure **2** (Scheme 1) suggested for this adduct is based mainly on the NMR spectrum, namely, the appearance of a doublet of quartets at δ 5.73 (J_{PH} = 25 and $J_{H\text{-}CH_3}$ = 1.5 Hz), significant for a 2-vinyl phosphol-2-enic proton as well as the expected methyl signals at δ 1.13s (C_{3a}-Me), 1.71 brs (C_5, C_6-two Me's), and 2.03 dd (J_{PH} = 2.5 and J_{HH} = 1.5 Hz, C_3-Me).



Scheme 1.

The second reaction performed was with 3,4 - dihydro - 1 - vinyl - 6 - methoxy - naphthalene which has been previously used by us with phosphol - 2 - en - 4 - one in the synthesis of a 17-phospha-steroid.[5] Prolonged heating of the reactants (7 days in a refluxing benzene solution) gave two main compounds which could be separated chromatographically. The spectral data of the first adduct **3**, $C_{25}H_{27}OPS$ m.p. 158°, λ_{max}^{EtOH} 275 nm (ϵ − 17,000), agree with a phosphasteroid structure. The NMR spectrum of **3** similar to that of compound **2**, showed the peculiar 2-phospholene vinyl proton at δ 5.80 dq(J_{PH} = 24 and J_{HH} = 1 Hz) as well as a saturated Me-group at δ 1.40s, and a phosphorus coupled vinyl methyl group at δ 2.15 brs. Surprisingly no other olefinic proton, except for the C-16-H could be seen in the NMR, and this observation together with the 275 nm (ϵ − 17,000) absorption known for Δ^8-estranes[6] supposes a similar double bond location in **3**. Four isomers can be suggested for adduct **3** namely, two 17-phospha, as well as two 15-phospha epimers. Oxidation of **3** with H_2O_2 (P=S to P=O transformation) gave a mixture of two phosphine oxides **3a** and **3b** as could be seen from the Me-group signals in the NMR spectrum (δ 1.40; 2.15 and δ 1.65; 1.95 respectively). One of the two isomers (**3a**) undergoes rapid rearrangement to its counterpart (**3b**)† during filtration of the mixture through a short alumina column. In the UV spectrum of **3b**, the 275 nm (ϵ − 17,000) absorption (of **3**) is bathochromically shifted to a less intensive absorption at λ_{max}^{EtOH} 280 nm (ϵ − 4500), the latter being in accordance with the long wave absorption of unconjugated anisole derivatives.[6] Thermal isomerization of **3** (24 h at *ca.* 180°, neat) resulted in a similar mixture to the one obtained upon oxidation (δ 1.40; 2.15 for **3** and δ 1.65; 1.85 for the new isomer **4**). Compound **4**, separated by preparative TLC,† showed similar δ-values for the Me-groups as the ones of the stable phosphine oxide isomer (**3b**) (*vide supra*) as well as a similar UV absorption (λ_{max} 277 nm; ϵ − 4800). These above described two rearrangements can be best rationalized by a $\Delta^{8(9)}$ to $\Delta^{8(14)}$ shift which is well known in the steriod field.[8] The interpretation of the latter observation is that **3** is a 15-phospha-steroid having a 14-proton, enabling the

†The purity of compounds **3b** and **4** is estimated as ≥90%. In the NMR spectrum of both compounds appears a new two proton multiplet, at ca. 3.25 ppm, which is attributed to the C-7 two protons.

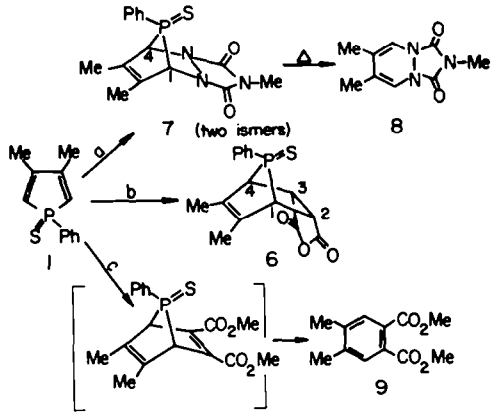
proposed $\Delta^{8(9)} \rightarrow \Delta^{8(14)}$ isomerization, rather than the 17-phospha isomer which has a 14-Me-group.

The second product of this cycloaddition reaction (**5**); m.p. 202°, $C_{25}H_{27}OPS$, λ_{max}^{EtOH} 268 nm (ϵ – 14,600), does not seem to be an isomeric phosphasteroid. The only olefinic proton observable in the NMR spectrum of **5**, a phosphorus uncoupled triplet at δ 5.50 (J = 6 Hz), can be best rationalized by a C-2-proton of a 1-substituted 3,4-dihydro-6-methoxy naphthalene; thus, indicating the latter moiety to be part of molecule **5**, an assumption which is also in accordance with the UV spectrum (*vide supra*). These observations, together with the absence of the easily recognizable 2-phospholenic vinyl proton and still existing two vinyl Me-groups, suggest compound **5** to be the 7-phosphabicyclo[2.2.1]heptanic-structure, i.e. the adduct of **1** entering the reaction as a diene.

Outstanding in the NMR spectrum of **5** was the P-uncoupled proton signal at δ 4.55 m which can be best attributed to the C-2 proton, expected to be coupled only to a small extent with the P-atom, because of a dihedral PCCH angle of *ca.* 90°.[9] Indeed, the C-2 proton should be paramagnetically shifted by the P=S group[1] even though it is not expected to be down field shifted to such an extent. Supporting evidence for structure **5** was obtained from its CMR spectrum which was further compared with that of several model compounds among which were compounds **6** and **7** synthesized from **1** using the corresponding dienophiles (Scheme 2). Adduct **6** was obtained as a single isomer, m.p. 157°, whereas 4-methyl triazolindione[18] gave two isomers, the ratio of which was found to be temperature dependent. One of the P-epimers m.p. 128° could be purified.

Attempts to crystallize the other epimer only resulted in elimination of the Ph–P=S group to give compound **8**. A similar extrusion was observed while reacting **1** with dimethyl acetylenedicarboxylate; the compound isolated was dimethyl-4,5-dimethyl phthalate **9**, rather than the expected adduct.

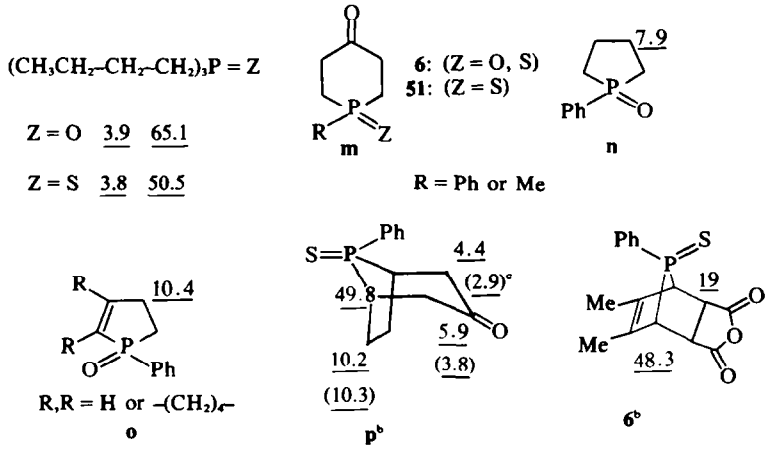
The CMR spectrum of **5** showed, at high field, nine carbons with the expected multiplicities (off-resonance experiment) namely, three methyls (14.24, 16.18 and 55.02 (OCH_3)), three methylenes (23.36, 27.78d (J_{PC} = 11.7 Hz) and 28.67) and three methines (37.15d (J_{PC} = 20.5), 49.97d



Scheme 2.

(J_{PC} = 49.8) and 53.43d (J_{PC} = 45.4)). Most significant in this CMR spectrum are the J_{PC} coupling constants: The sensitivity of ^{13}C–^{31}P couplings to substituent and structural effects is quite well known.[10] Furthermore, while the $^1J_{PC}$ in phosphine oxides and sulfides is relatively insensitive to the structural features (a $^1J_{PC}$ value of *ca.* 50 Hz is observed for all the phosphine sulfides mentioned herewith) the $^2J_{PC}$ is much more influenced. Comparison of compounds **13–17** (Table 1)[11,12] indicates that the conversion from an aliphatic oxide (or sulfide) to the 6 membered ring compounds (**14**, **17**) does not affect the $^2J_{PC}$ significantly. There is an increase in coupling in contracting the ring to the phospholane (**15**) and a further increment when turning to the more strained phospholene (**16**). The structure dependence is brought clearly into account, in compound **17** where the J_{PC} coupling for C_6, C_7(10.3 Hz) is larger than that of C_2, C_4 (2.9 Hz). The large $^2J_{PC}$ value of 19 Hz measured for compound **6** may result from the rigid bicyclic skeleton on one hand, and the substitution effect,[12] expected to increase this value, on the other hand.

Table 1. J_{PC} values of several phosphine oxides and sulfides.[a]



[a] For compounds **13–16**, see references 11–12.
[b] Measured at 22.63 MHz in $CDCl_3$ solution with respect to TMS.
[c] The values in parentheses are for the equatorial P-phenyl isomer.

Considering the above data, the $^2J_{PC_2}$ (20.5 Hz) and $^2J_{PC_5}$ (11.7 Hz) observed in case of **5** are in good agreement with the proposed structure.

Oxidation of **5** with 1 equivalent of m-chloroperbenzoic acid gave only one oxide which seems to have the same P-configuration as in compound **5**, based on an almost identical NMR spectrum. Complexation of the latter with $Eu(fod)_3$[13] suggests the proposed P-configuration of **5** (the C-2, C-2' protons are much more shifted than the C-5, C-6 Me-groups).

Although compound **1** seems to prefer the addition in which it participates as a diene, the above described cycloaddition reactions demonstrate clearly the availability of phospholsulfides as dienes, as well as dienophiles.

The last reaction to be discussed is the one between **1** and thioketones. While performing the reaction between **1** and an oxyallyl cation an unexpected compound was obtained apart from the $[2\pi + 4\pi]$ cycloaddition adduct.[2] A possible mechanism leading to this compound involves an intramolecular cycloaddition reaction between the phospholenic moiety and the thioketone group. In order to check this possibility the reaction of phospholsulfide with several thioketones known as excellent dienophiles was undertaken. Reaction of thioacetophenone[19] with **1** gave an adduct (**10**); m.p. 160°. Whereas the mass spectrum of **10** is in full agreement with the tentatively suggested 2-thio-7-phosphabicyclo[2.2.1]heptane, the interpretation of the methyl group signals seen in the NMR spectrum was not obvious. The two signals at δ 0.73 and δ 1.56 are attributed, by us, to the C_5, C_6 methyl groups, based on their $^4J_{PH}$ coupling constant, thus leaving the δ 2.56 singlet for the C-3-methyl group. *A priori* the C-5-methyl group is expected to give rise to a signal at $\delta \simeq 1.0$ ppm[2] and the C-3-methyl at $\delta \simeq 2.0$.† The lower value found for the former signal, and the higher one found for the latter may be both explained by a twisted bicyclo[2.2.1]heptane which will thus bring the 5-methyl closer to the diamagnetic region of the 3-phenyl ring and the 3-methyl closer to the paramagnetic shifting P=S group.‡ To ascertain this assumption the synthesis and spectra of some additional compounds of this series is now under investigation.

Of interest was the reaction between thiophosgene and **1**. Thiophosgene is known to react with cyclopentadiene to give a 2-thiobicyclo[2.2.1]-heptane;[16] work-up of our reaction mixture, however, gave a product without the sulfur atom.

Structure **12**, 1 - phenyl - 1 - oxo - 3 - methyl - 4 - methylene - phosphol - 2 - ene, is the one proposed for this compound, the formation of which proceeds most likely through intermediate **11** (Scheme 1). Indeed it was found that in the absence of water such an intermediate could be isolated. The addition of one drop of thiophosgene to a solution of **1** in $CDCl_3$, in an NMR tube, brought about the

†This value is deduced by comparison with 4,6 - dimethyl - 6 - phenyl - 1 - thia - cyclohex - 3 - ene[15] and taking into account the anisotropic effect of the P=S group.[1]

‡The twisted compound may also explain the two different $^1J_{PH_1}$ and $^1J_{PH_4}$ values (4.5 and 6 Hz).

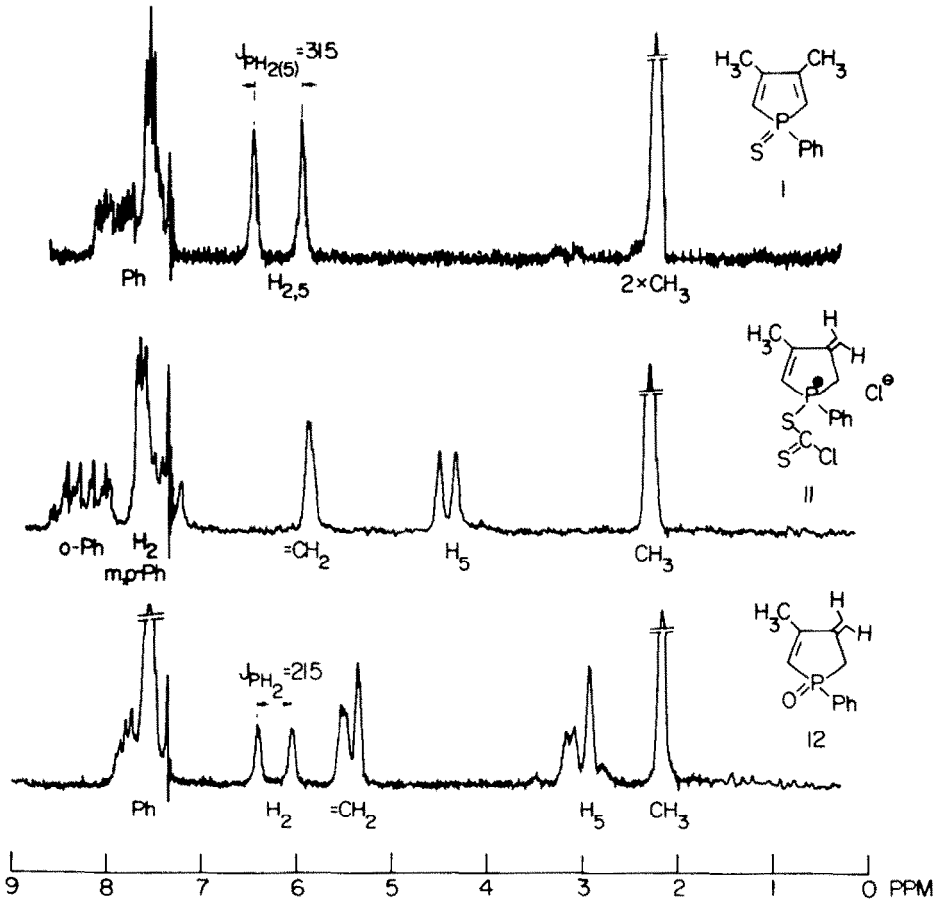


Fig. 1. NMR spectra of **1**, intermediate **11** and **12**.

formation of the P^{IV}-intermediate **11**. This formation was complete after *ca* 60 min at 32°. Moreover monitoring the NMR spectrum revealed the same rate for the formation of the positive charged P-atom, as well as the tautomerisation leading to the external methylene group.†

The formation of the positive charge on the P-atom, could be best followed by the strong paramagnetic shifts of the neighbouring C_2 and C_5 protons as well as the *ortho*-phenyl ones (Fig. 1).‡ The P=S to P=O transformation using $CSCl_2$ may find its synthetic applications when one faces the need of preventing oxidations of other sensitive sites in a molecule.

The scope of the cycloaddition of phospholes other than **1** with dienes directed mainly towards the synthesis of phosphasteroids is under further investigation.

EXPERIMENTAL

M.ps were taken on a Unimelt Thomas and Hoover Capillary m.p. apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Infracord model 337 spectrophotometer. ^{1}H-NMR spectra were taken on a Jeol JMN-C-60 HL spectrometer, and ^{13}C-NMR on a Bruker WH-90 instrument, for 5–10% soln in $CDCl_3$, containing TMS as an internal standard. Mass spectra were taken on a Du-Pont 21-491B instrument. UV spectra were recorded on a Cary-14 spectrophotometer. 3,4 - Dimethyl - 1 - thio - 1 - phenylphosphole was prepared according to Mathey *et al.*[3]

Phenyl - 1 - thio - 3,3a,5,6 - tetramethyl - 3a,4,7,7a - tetrahydro - 1(H) - phosphindole (**2**)

A soln of 3,4 - dimethyl - 1 - thio - 1 - phenylphosphole (1 g) and excess 2,3 - dimethylbutadiene (4 g) in p-xylene (20 ml) was heated for 12 hr at 140° in a sealed tube under N_2. After removing the solvent and the unreacted butadiene under reduced pressure, the obtained dark, viscous oil was chromatographed on a neutral alumina column. Elution with benzene–chloroform (1:1) yielded pure **2** (400 mg). Compound **2** could not be crystallised; $\nu_{max}^{CHCl_3}$ 3050, 2950, 1600, 1450, 1400, 1100, 950, 835 cm; (Found: M^+ 302 (100%); $C_{18}H_{23}PS$ requires: MWt 302); *m/e* (%): 302 (100), 287 (27), 147 (26) and 105 (25); δ 1.13s (C-3a-Me), 1.71 m ($\Delta W_{1/2}$ = 5.5, C-5 and C-6 two Me's), 2.03dd (J_{PH} = 2.5 and J_{HH} = 1.5 Hz) and 7.25–8.0 m (Ph).

3 - *Methoxy* - 15 *phenyl* - 15 - *thio* - 17 - *methyl* - 15 - *phospha* - 1,3,5(10),8,16 - *estrapentaen* (**3**) *and* 2 - *exo*(3',4' - *dihydro* - 6' - *methoxy* - *naphthyl*) - 5,6 - *dimethyl* - 7 - *phenyl* - 7 - *thio* - 7 - *phosphabicyclo*[2.2.1]*hept* - 5 - *ene* (**5**)

A soln of 3,4 - dimethyl - 1 - thio - 1 - phenylphosphole (3.7 g) and 1 - vinyl - 6 - methoxy - 3,4 - dihydronaphthalene (5 g) in benzene (25 ml) was refluxed for 7 days under N_2. Upon cooling of the soln, compound **5** (1.5 g) crystallised out. The residue after evaporation was chromatographed on a silica gel column (Merck 7734). Elution with benzene with raising percentage of chloroform yielded first pure **3** (0.7 g) and then more of **5** (1 g). Compound **3** was recrystallised from EtOAc, m.p. 158°; ν_{max}^{KBr} 2930, 1610, 1500, 1430, 1305, 1250, 1140, 1050 cm^{-1}; λ_{max}^{EtOH} 275 nm (ϵ – 17,000); δ 1.40s (C-13-Me), 2.15 brs (C-17-Me), 3.78s (OMe), 5.83 dq (J_{PH} = 24 and J_{HH} ≃ 1 Hz, C-16-H), 6.6d (J = 3 Hz, C-4-H), 6.7dd (J = 3 and 7.5 Hz, C-2-H) and 7.0–7.96 (6 H). *m/e* (%): 406 (40), 374 (100), 359 (18) 319 (4) and 265 (30). (Found: C, 73.73; H, 6.50; P, 7.59; S, 7.75. $C_{25}H_{27}OPS$ requires: C, 73.87; H, 6.69; P, 7.62; S, 7.86%). Compound **5** was recrystallised from benzene or EtOAc, m.p. 202°–203°; ν_{max}^{KBr} 2900, 2795, 1600, 1560, 1490, 1430, 1235, 1120, 1107, 810, 680 cm^{-1}; λ_{max}^{EtOH} 268 mm (ϵ – 14,600); δ 1.34 brs (Me), 1.64 brs (Me), 3.85s (OMe), 4.55m (C-2-H), 5.50 brt (J = 6 Hz, C-2'-H), 6.24 brs (C-5'-H), 6.82dd (J = 7.5; 2.5, C-7'-H) and 7.3–7.8 (6H). (Found: C, 73.71; H, 6.59; P, 7.79; S, 7.89. $C_{25}H_{27}OPS$ requires; C, 73.87; H, 6.69; P, 7.62; S, 7.86%).

Oxidation of compound **3**

To a soln of **3** (70 mg) in $CHCl_3$ (3 ml), a 30% H_2O_2 soln (3–4 drops) was added, followed by addition of acetone until the soln became homogeneous. The mixture was stirred at r.t. for 4 days, then chloroform (25 ml) was added and the soln was washed with 5% $FeSO_4$ aq. until a negative KI test. After evaporation of the dried soln (Na_2SO_4) a 1:1 mixture of **3a** and **3b** was obtained. Filtration of the mixture through a short alumina column gave mainly compound **3b** ≥ 90% purity. δ 1.65s (Me), 1.95brs (Me), 3.30m (C-7-2H), 3.90s (OMe), 5.95dq (J_{PH} = 18, J_{HH} ≃ 1 Hz, 1 H).

Thermal isomerization of **3**

Heating of compound **3** (100 mg) at ~180° for 24 h, gave a 1:1 mixture of **3** and **4**. Preparative TLC gave isomer **4** in ≥90% purity; δ 1.65s (3H), 1.85s (3H), 3.20m (C-7-2H), 3.80s (OMe), 5.85dq (J_{PH} = 24, J_{HH} ≃ 1 Hz, C-16-H).

Maleic anhydride adduct (**6**) *of* **1**

A soln of **1** (230 mg) and maleic anhydride (100 mg) in CH_2Cl_2 (10 ml) was stirred for 24 h at r.t. The solvent was removed and the residue crystallised from ether–acetone; m.p. 157°; ν_{max}^{KBr} 1860, 1790, 1440, 1210, 1120, 980, 770, 740, 725, 705, 665 and 590 cm^{-1}; δ 1.60d (J_{PH} = 3 Hz, C-8, C-9 two Me's), 3.52dq (J_{PH} ≃ J_{HH} = 2 Hz, 2H) and 4.43dt (J_{PH} ≃ 1; J_{HH} = 2.5, 2H) and 7.4–7.7m (Ph). (Found: C, 60.40; H, 4.80. $C_{16}H_{15}O_5P$ requires: C, 60.38; H, 4.75%, MWt 318). *m/e* (%); 318 (40), 220 (66), 140 (100).

4 - *Methyl* - 1,2,4 - *triazolin* - 3,5 - *dione adduct* (**7**) *of* **1**

A soln of the triazolindione[18] (250 mg) in CH_2Cl_2 (2 ml) was rapidly added to a cooled (–30°) stirred soln of **1** (440 mg) in CH_2Cl_2 (20 ml). The mixture was stirred for 3 h at –30° and then allowed to warm up slowly to 0°. Evaporation of the solvent gave a 1:1 mixture of two adducts. Performing the reaction at r.t. gave mainly one isomer (**7**); m.p. 128° (acetone-ether); ν_{max}^{KBr} 3030, 2980, 1780, 1760, 1440, 1395, 1190, 1100, 1040, 1010, 750, 610, 550 cm^{-1}; δ 1.75d (J_{PH} = 1.5, two Me's), 3.13s (N–Me), 5.18d (J_{PH} = 1.5 Hz, bridge head-2H) and 7.35–7.60m (Ph); and δ 1.88d (J_{PH} = 1.5, two Me's), 3.13s (N–Me), 5.10d (J_{PH} = 4 Hz) for the unstable isomer. *m/e* (%): 248 (5, M-PhPS) 193 (63), 178 (2), 108 (87), 88 (35), 61 (100). Attempts to crystallize the unstable isomer resulted in compound **8**; m.p. 235° (EtOH); ν_{max}^{KBr} 2900, 1780, 1760, 1450, 1110 cm^{-1}. 1.78d (J_{PH} = 2 Hz two Me's) 3.18s (N–Me) and 6.63brs (2H). (Found: *m/e* 248, $C_7H_{11}N_3O_2$ requires: MWt 248); mass spectrum identical with that of **7**.

The reaction product (**9**) *of dimethyl acetylenedicarboxylate and* **1**

A soln of **1** (440 mg) and dimethyl acetylenedicarboxylate (300 mg) in benzene (10 ml) was stirred for 24 h at r.t. The solvent was removed and the residue crystallized from petrol–ether; m.p. 47°–49°; ν_{max}^{neat} 2920, 1730, 1430, 1300, 1150, 1120, 1025, 880 cm^{-1}; δ 2.22s (2Me's), 3.82s (2OMe's) and 7.42s (2H); *m/e* (%): 222 (M^+, 91), 191 (100), 163 (23), 104 (28).

3,5,6 - *Trimethyl* - 3,7 - *diphenyl* - 7 - *thio* - 2 - *thia* - 7 - *phospha* - *bicydo*[2.2.1]*hept* - 5 - *ene* (**10**)

Thioacetophenone[19] (300 mg) was added in portions to a soln of **1** (440 mg) in chloroform, under N_2, at 55° during 48 h. After evaporating the solvent under reduced pressure, the obtained oil was chromatographed on a neutral alumina column. Elution with CCl_4 yielded pure **10** (100 mg); m.p. 160°; ν_{max}^{KBr} 2970, 2930, 1440, 1130, 780, 740 cm^{-1}; δ 0.73brs (J_{PH} ≃ 1 Hz, C-5-Me), 1.56brs (J_{PH} ≃ 1 Hz, C-6-Me), 2.55s (C-3-Me), 3.28dd (J_{PH} = 4.5 and J_{HH} = 1.5, 1H), 3.93dd (J_{PH} = 6, J_{HH} = 1.5, 1H) and 7.2–7.8 (2 Ph's). *m/e* (%): 356 (13, M^+; $C_{20}H_{21}PS_2$), 220 (88, M-C(S)PhMe), (100, M-PhPS) and 136 (18, C(S)PhMe).

†A similar tautomerization was observed by Mathey using CF_3CO_2H;[17] addition of conc. HCl to **1** in $CDCl_3$ instead of $CSCl_2$, did not however affect the compound.

‡A similar shift could be observed for 1-phenyl-phospholene sulfides whereas the corresponding oxides were not influenced. Thiophosgene can, thus, be used as an NMR shift reagent for the vicinal to P=S protons of phosphine sulfides which are hardly complexed by Eu(fod)$_3$.

1 - *Phenyl* - 1 - *oxo* - 3 - *methyl* - 4 - *methylene* - *phosphol* - 2 - *ene* (**12**)

Thiophosgene (0.3 ml, freshly distilled) was added to a soln of **1** (200 mg) in chloroform (4 ml). The mixture was stirred for 2 h at r.t. then chloroform (10 ml) was added and the soln was washed with 5% $NaHCO_3$ aq, H_2O, dried and evaporated. Filtration of the residue through an alumina column gave pure **12**; m.p. 67°–69°; δ 2.15brs (C-3-Me), 3.0m (C-5-2H), 5.35brs and 5.50m (=CH_2), 6.21d (J_{PH} = 22, C-2-H) and 7.4–7.8 (Ph). *m/e* (%): 204 (100, M$^+$). (Found: C, 70.65; H, 6.55; P, 15.30. $C_{12}H_{13}OP$ requires: C, 70.58, H, 6.41, P, 15.17%).

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