A ^{31}P NMR STUDY OF REACTIONS OF 2,3-BIS(DIPHENYLPHOSPHINO)-6-PHENYL-λ^3-PHOSPHININE WITH SULFUR: FORMATION, CHARACTERIZATION, AND FURTHER REACTION OF A STABLE PHOSPHININE 1-SULFIDE

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Abstract- The reactions of 2,3-bis(diphenylphosphino)-6-phenyl-λ^3-phosphinine with sulfur at room temperature and at elevated temperatures are discussed. Among the products formed is 2-diphenylphosphino-3-diphenylthiophosphinyl-6-phenylphosphinine 1-sulfide, a rare example of a relatively stable heterocycle containing $\sigma^3 \lambda^5$ phosphorus. The route whereby this is formed and its subsequent reaction with traces of H_2S slowly generated in the reaction medium are also discussed in the light of nmr evidence.

INTRODUCTION

Low-coordination phosphorus compounds, usually very highly reactive and transient species, are of considerable current interest and structures containing $\sigma^1 \lambda^3$ (eg RC≡P), $\sigma^2 \lambda^3$ (eg R_2C=PR'), and $\sigma^3 \lambda^5$ (eg 1) phosphorus have all been reviewed over the past few years.[1-3] Considering the last of these categories, very few phosphaalkene sulfides such as 1 have been reported[3] and very few heterocycles containing $\sigma^3 \lambda^5$ phosphorus are known. We report here the synthesis and some chemistry of a phosphinine 1-sulfide which is a heterocyclic analogue of a phosphaalkene sulfide. Only one brief report of such a species (in this case, a transient species) has appeared previously[4] and characterization was incomplete.

RESULTS AND DISCUSSION

In earlier work, we reported[5] the synthesis of 2,3-bis(diphenylphosphino)-6-phenyl-λ^3-phosphinine (2) and some discussion regarding the origin of the extraordinarily high value of $^3J_{P^2P^3}$ (178 Hz) exhibited by this compound was

presented. As part of an investigation of this large coupling constant, reactions of the side-chain phosphorus atoms of 2 with a variety of reagents, mainly transition metal salts, were studied and reported[5] but the reactions with sulfur were found to be very complex and they became the focus of a separate investigation, the results of which are reported here.

The products isolated, or easily characterized, from reactions of 2 with sulfur depend upon the conditions. Thus, if the reaction is carried out in boiling benzene, the isolable products are mainly 3 and small amounts of 4a. If, however, the reaction mixture is stirred at room temperature, mainly 3 but also significant amounts of a phosphinine 1-sulfide 5a or 5b (ca 20%) are formed. While unreacted 2 and sulfur can be removed from the mixture by chromatography on silica gel, 3 and the phosphinine sulfide cannot be separated although it is noteworthy that the latter survives this procedure and presumably owes its

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2

3

4a, R = H$_b$

4b, R = OMe

5a, R = P(S)Ph$_2$,
R' = PPh$_2$

5b, R = PPh$_2$,
R' = P(S)Ph$_2$

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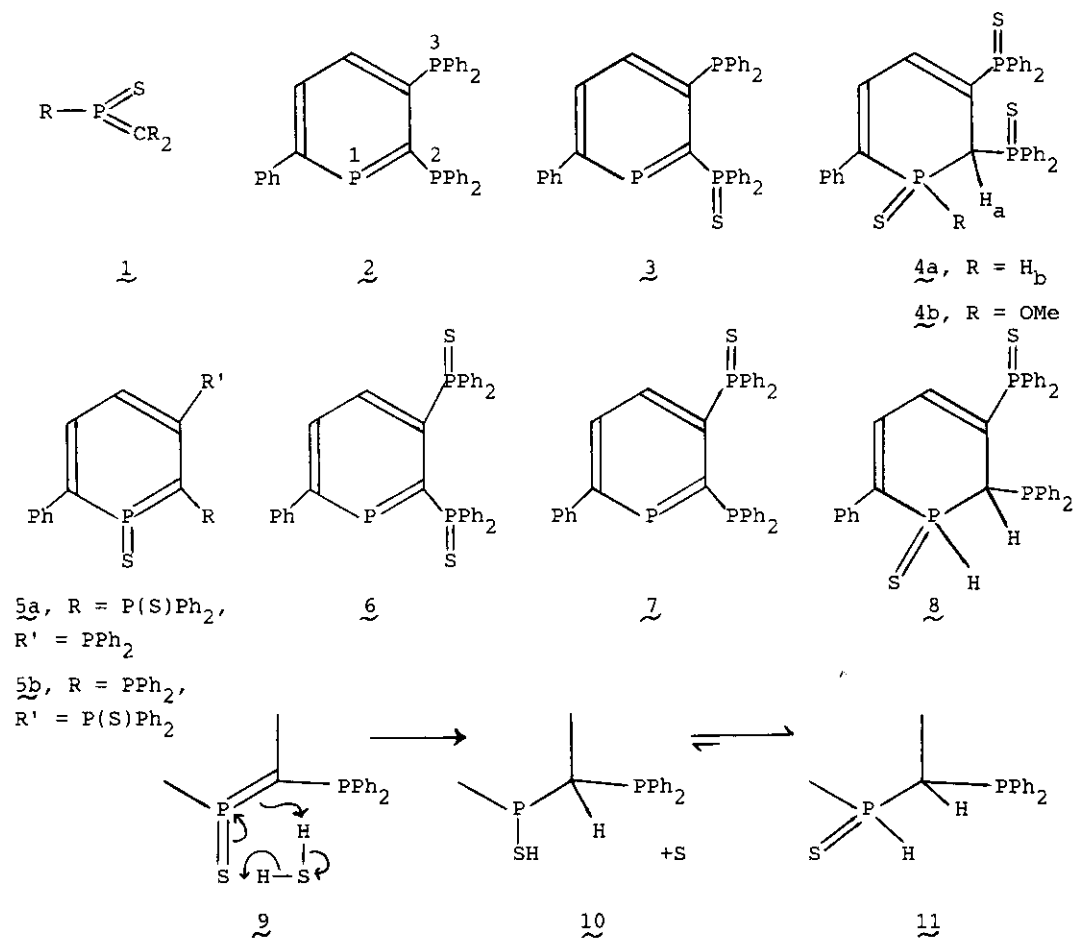
unusual stability to the heavy substitution around the —P(S)=C portion of the molecule. Under these conditions, no 4a is formed unless the mixture is stirred for several days and as the amount of 4a increases, that of 5a or 5b decreases. Hence, 4a is formed from the phosphinine sulfide and this will be discussed further later. The phosphinine sulfide also reacts slowly with methanol, in the expected manner, to give 4b. Reactions of 2 with selenium follow a similar course.

The substance of the results outlined above, including full spectroscopic characterizations, has been the subject of a preliminary communication.[6] Details of synthetic procedures, briefly referred to in the preliminary report, and some ^{31}P and ^{1}H nmr data are given in the experimental section.

What was not clear from the preliminary study are the interrelationships between the various products and the situation is complicated by the fact that the phosphinine 1-sulfide has defied all attempts to isolate it as a pure compound. Much information can be gained, however, from a detailed ^{31}P nmr study. For example, while it would be a natural assumption that the phosphinine sulfide is 5a, derived from 3, this is clearly not the case since ^{31}P nmr examination of a mixture of 3 (obtained from the reaction of 2 with sulfur in hot benzene and purified by chromatography on silica gel) and sulfur stirred at room temperature in benzene for several days shows that no reaction occurs. It would seem highly probable then that the phosphinine sulfide is 5b unless, in the sequence of reactions leading to the phosphinine sulfide, it is the ring phosphorus atom of 2 which acquires sulfur before the side-chain P atoms. This, however, is unlikely given the very poor nucleophilic characteristics noted earlier[7] for the ring P atom of λ^3-phosphinines and the slowness with which less heavily substituted λ^3-phosphinines react with sulfur.[4]

Compounds containing low-coordinate phosphorus are characterized by large downfield shifts. Thus, the λ^3-phosphinine 2 shows δ ^{31}P at 224.8 (in benzene) while the phosphinine 1-sulfide 5b and 3 show signals at δ 248.8 and 218.5 respectively. Since there are seven species containing low-coordinate phosphorus which could be formed by reaction of 2 with sulfur (ie any or all P atoms bearing sulfur) it should be a simple matter to determine how many and, perhaps, which of these are produced and consumed during the reaction by monitoring the nmr spectrum of a mixture of, initially, pure 2 and sulfur over an extended period.

Such an experiment carried out over a period of four days with spectra being recorded every 6-12 hours shows that apart from 2, 3 and 5b already character-ized, only one additional species containing low-coordinate phosphorus is present in the reaction mixture for any length of time. This shows the ring phosphorus atom at δ [31]P = 233.3 with one very large coupling (113 Hz) and one very small coupling (4 Hz) to the remaining P atoms. The couplings are similar to those observed (110.5 Hz and 8.5 Hz)[6] for 3 and are consistent[6] with the presence of a non-bonding pair upon the ring P atom. Examination of the remainder of the spectrum shows that the only signals present for phosphorus atoms to which sulphur is not attached are associated with 2, 3 and 5b. In addition, a signal consisting of two unresolved narrow multiplets centered upon δ 50.1 is the only signal in the spectrum not attributable to the side chain P atoms of 2, 3 or 5b. Thus, in the new species, it appears that both side-chain P atoms bear sulfur while the ring P atom does not and the structure is therefore the very crowded system 6. The two unresolved multiplets presumably arise from the AB portion of an ABX spectrum in which J_{AB} is of similar magnitude to δA–δB as is observed[5] in the spectrum of 2 itself. The amount of 6 present, while always small, increases slowly with time and the molecule shows no signs of reacting further with sulfur. Since it has been shown (see earlier discussion) that 3 does not react with sulfur, the precursor to 6 must be 7 which is consumed about as fast as it is generated since no other significant peaks are observed in the δ 200-250 range. The same argument applies to the formation of the phosphinine sulfide 5b which, since it is not formed from 3, must be formed from 7. Thus, for reasons which are not clear, 7 is considerably more reactive than 3 both at the remaining side-chain tertiary P atom and the ring P atom.

It should, perhaps, be mentioned that acyclic phosphaalkene sulfides add sulfur[8] across the P—C linkage to give a three-membered ring. No evidence was observed in the spectroscopic study reported here that 5b does this unless a very weak, but long-lived, triplet (J ≈15 Hz) at δ 62.4 is associated with such a species. This seems unlikely, however, since δ ^{31}P for the ring P atom of these systems is normally[8] in the range δ = 2-7 and there are apparently no other signals in the spectrum of the mixture associated with the peak at δ 62.4.

The second facet of this study investigated by ^{31}P nmr methods was the route whereby 5b is converted into 4a. If mixtures of 2 and sulfur are heated

under reflux in benzene, small amounts of 4a (ca 11%) are formed in about 3 h with the major product being 3 (68%). If the reaction is carried out at room temperature, 4a becomes a significant product only after 5-6 days and the amount of 4a present increases as that of 5b decreases. The fact that 4a and 5b differ by the elements of H_2S suggested that small amounts of the latter (probably formed by slow hydrolysis of sulfur by traces of moisture) may add to 5b to give 4a. This indeed appears to be the case since if a small quantity of H_2S is added to a reaction mixture of 2 and sulfur which has proceeded to the stage where it contains only 3, 5b, 6 and a little sulfur, formation of 4a is significantly faster than if the mixture is left to stand in the absence of H_2S.

Nmr evidence indicates that the reaction proceeds in two stages. Thus, ^{31}P nmr examination of a mixture of 2 and sulfur in benzene which has been allowed to stand for several days shows the absence of 2 and the presence of a large amount of 3 together with small amounts of 5b and 6. In addition, there is in the spectrum a new weak doublet of doublets (J = 14 and 21 Hz) at δ = 10.1 together with a second doublet of doublets at δ = -4.8 (J = 6 and 14 Hz). There is evidence of a third signal under the complex multiplet of $Ph_2P=S$ signals arising from 3, 5b, and 6 centred on δ = 45 but this could not be resolved from the other signals in the region. This pattern is consistent with structure 8 with the signal at δ -4.8 arising from the side-chain diphenylphosphino group and the signal at δ 10.1 arising from the ring P atom, the shift of which is similar to that of the ring P atom in 4a.[6] The coupling constants are also similar to those observed[6] for 4a. That this interpretation is probably correct is shown by the fact that as more time passes, these signals diminish and the signals character-istic[6] of 4a ($δP^1$ 8.6, $δP^2$ and $δP^3$ 38.6 and 48.9; $^2J_{P^1P^2} = {}^3J_{P^1P^3}$ = 17.1 Hz, $^3J_{P^2P^3}$ = 4.9 Hz) grow. It appears then that the first step in the conversion of 5b into 4a is the reduction of the P—C linkage in 5b as outlined in the sequence 9 → 10 → 11, with the phosphaalkene sulfide portion of the molecule acting similarly to a 1,3-dipole, and this is followed by uptake of sulfur by P^2 in 8. The normal type of reaction of a phosphaalkene sulfide with a polar molecule is[3] direct addition across the P—C linkage as is observed[6] with 5b and methanol to give 4b.

Despite this detailed nmr analysis, several points remain unresolved. For example, it has not been established conclusively that 7 is an intermediate

although no reasonable alternative comes to mind. Also, if 7 is indeed a transi-
ent intermediate, it is not at all obvious why it is so much more reactive
towards sulfur than is 3. However, the broad sequence of reactions has now been
established.

EXPERIMENTAL

^{31}P and ^{1}H nmr spectra were recorded at ambient temperature in $CHCl_3$ (for pure
compounds) or C_6H_6 (for reaction mixtures) using a Bruker WP80 FT spectrometer
and an external D_2O lock (capillary) with 85% H_3PO_4 and TMS as the external and
internal references respectively. Shifts downfield of the reference are posi-
tive. Mass spectra were obtained using an Hitachi Perkin-Elmer RMU-7 double
focusing mass spectrometer (direct inlet) at 80 eV. Carbon and hydrogen micro-
analytical data were collected in these laboratories using a CEC model 240XA
elemental analyzer with vanadium pentoxide used as a combustion aid. Microana-
lytical data for sulfur were acquired, also in these laboratories, using an
Alphamatic sulfur analyzer. Column chromatography was carried out by the dry-
column method using silica specially prepared for this process and obtained from
ICN Pharmaceuticals, Inc., K&K Laboratories Division. 2,3-Bis(diphenylphosphino)-
6-phenyl-λ^3-phosphinine (2) was prepared as previously reported.[5] Melting points
were taken using a sealed capillary and a Gallenkamp melting point apparatus and
are uncorrected.

Time-dependent nmr studies. A typical procedure for those experiments in which
the ^{31}P spectrum of the reaction mixture was monitored over a period of time (see
discussion) is as follows. The phosphinine 2 (0.25 g, 0.46 mmol) was dissolved
in dry, degassed benzene (50 ml) and to the solution was added S_8 (0.059 g, 0.23
mmol) (ie 4 S atoms per molecule of 2). The mixture was stirred magnetically
under nitrogen and every 6-12 hours, an aliquot was transferred to a 10 mm nmr
tube under nitrogen for immediate nmr examination. This procedure was continued
for up to 6 days. In some instances, where the reaction had proceeded to the
stage where only 3, 5b, and 6 (and a little sulfur) were present (2-3 days),
small amounts of H_2S gas were added to an nmr tube containing an aliquot of the
mixture and the rate at which 4a was formed from 5b was monitored.

Synthesis of 3-diphenylphosphino-2-diphenylthiophosphinyl-6-phenyl-λ^3-phosphinine

(3) and 2,3-bis(diphenylthiophosphinyl)-6-phenyl-1,2-dihydrophosphinine 1-sulfide

(4a). The phosphinine 2 (0.1 g, 0.185 mmol) was dissolved in benzene (ACS grade, 50 ml) and S_8 (0.0356 g, 0.139 mmol) was added. The mixture was then heated under reflux for 3 h, cooled, and concentrated to ca 2 ml under a stream of N_2. The resulting yellow solution was chromatographed (dry column) on silica gel (ca. 60 g) typically using, in sequence, 100 ml of each of the following C_6H_6/$CHCl_3$ mixtures: 1:1, 2:3, 1:2, 1:3, 1:4. This was followed by elution with pure chloroform (250 ml). This resulted in the formation of 4 bands on the column which were eluted and evaporated to give first unreacted sulfur (trace), then yellow crystals of 3 (0.072 g, 68%, mp 175-190°C, decomp.), followed by pale yellow crystals of 4a (13.1 mg, 11%, mp 147-148°C, decomp.) in significantly better yield than reported previously[6] and, finally, a small amount of unreacted phosphinine which was normally left on the column. Analytical and spectroscopic data are as follows:

For 3. Anal. Calcd for $C_{35}H_{27}P_3S$: C, 73.42; H, 4.75; S, 5.60. Found: C, 73.27; H, 4.96; S, 5.60. Nmr: δ ^{31}P 218.5 (dd, P^1), 45.0 (dd, P^2), -11.8 (dd, P^3); $^2J_{P^1P^2}$ 110.5, $^3J_{P^1P^3}$ 8.5, $^3J_{P^2P^3}$ 45.3 Hz. Ms: m/z 572 (M^+).

For 4a. Anal. Calcd for $C_{35}H_{29}P_3S_3$: C, 65.82; H, 4.58. Found: C, 66.07; H, 4.95. Nmr: δ^{31}P 8.6 (t, P^1), 38.6 (dd, P^2 or P^3), 48.9 (dd, P^2 or P^3); δ ^{1}H 3.28 (m, v. br., 1H, H_a), 7.18 (dm, 1H, H_b, $^1J_{PH}$ 527 Hz confirmed by proton-coupled ^{31}P measurements), 5.85-8.25 (m, 27H, aromatic/olefinic). Ms: insufficient thermal stability.

<u>Syntheses of 2-diphenylphosphino-3-diphenylthiophosphinyl-6-phenylphosphinine 1-sulfide (5b) and 2,3-bis(diphenylthiophosphinyl)-1-methoxy-6-phenyl-1,2-dihydro-phosphinine 1-sulfide (4b).</u> These syntheses have been reported elsewhere in general terms[6] and were carried out on the same scale as outlined above. Both compounds were obtained in conjunction with large quantities of 3 from which they could not be separated. Both were characterized spectroscopically and full spectroscopic details have also been reported elsewhere.[6]

ACKNOWLEDGEMENT

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