

The Insertion of Sulfur and Selenium into the 1,2-Dihydrophosphete Ring

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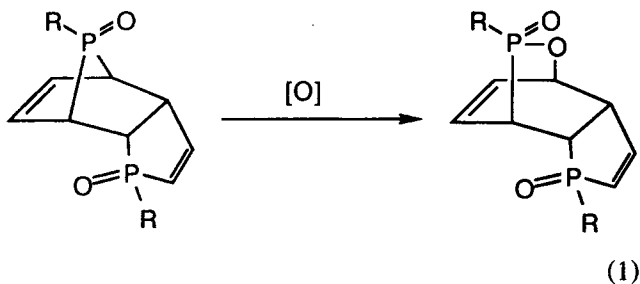
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ABSTRACT

Sulfur and selenium react with a 1,2-dihydrophosphete $P-W(CO)_5$ complex at ca. $120^\circ C$ to give the corresponding 2,5-dihydro-1,2-thiaphosphole and 2,5-dihydro-1,2-selenaphosphole complexes, respectively. These products result from an insertion of S or Se into the $P-C$ sp^3 bond of the four-membered ring.

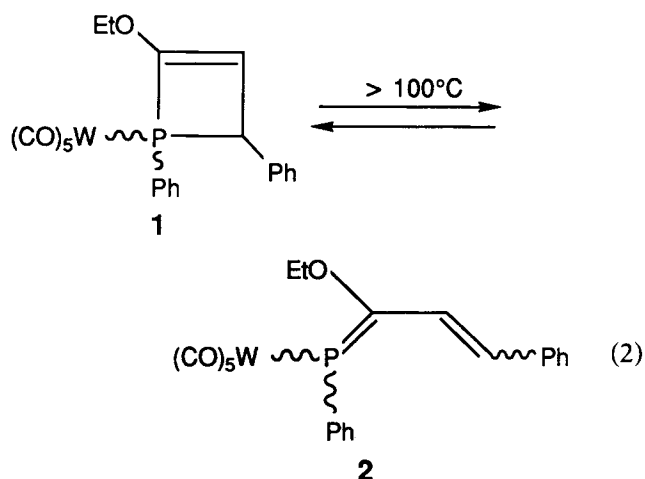
The controlled oxidative cleavage of $P-C$ bonds is well exemplified when these bonds are incorporated into strained rings. For example, Kashman [1] has demonstrated that it is possible to insert oxygen into one of the $P-C$ bridge bonds of phosphole oxide [4 + 2] dimers (Eq. 1) and Quin [2] has developed the chemistry of the resulting insertion products.



However, similar insertions involving sulfur and selenium are not as well known. We wish to de-

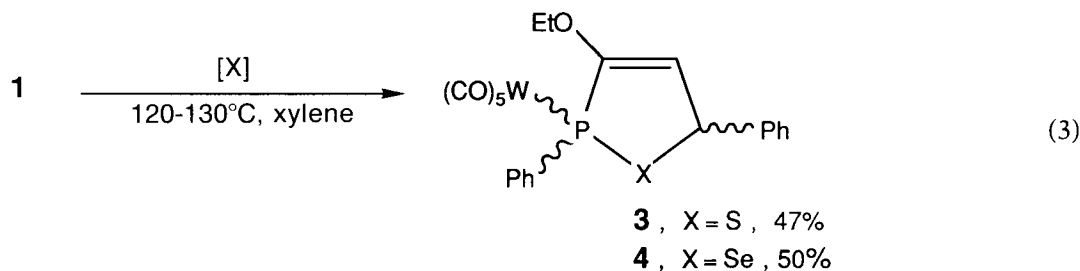
scribe a clearcut example of such an insertion into the very strained 1,2-dihydrophosphete ring.

On the basis of a X-ray crystal structure analysis, showing a very long $P-C$ sp^3 intracyclic bond [1.902 (5) Å] [3] and of various [4 + 2] cycloadditions with $C=C$, $C=O$, and $C\equiv C$ multiple bonds [4], we recently demonstrated that a complex such as **1** is in equilibrium with its open-chain isomer **2** above $100^\circ C$ (Eq. 2):



As a logical extension of these preliminary findings, we decided to carry out a systematic study of the various possible insertion reactions of the 1,2-dihydrophosphete ring. In so doing, we discovered that both sulfur and selenium were able to insert into the 1,2-dihydrophosphete complex **1** at ca. $120-130^\circ C$ without alteration of the $P-W(CO)_5$ complexing group (Eq. 3).

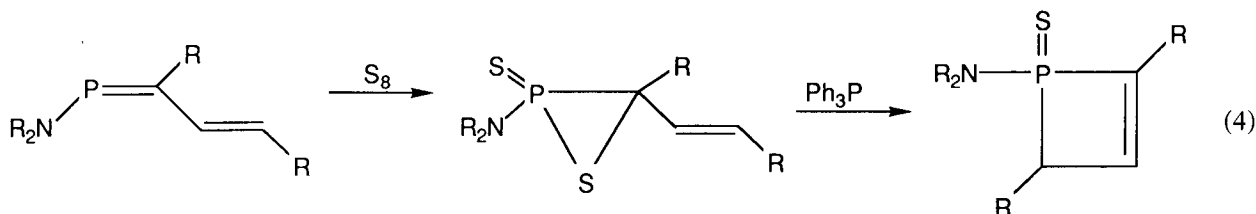
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The main spectral data corresponding to the isomeric mixtures of **1**, **3**, and **4** are collected in Table 1. The most significant results concern the ring sp^3 carbon. The 1J ($P\text{-CHPh}$) coupling constant in **1** is ca. 30–32 Hz, whereas the 2J ($P\text{-X-CHPh}$) coupling constants in **3** and **4** fall to 0 Hz. Very low values have been recorded in the literature for the 2J ($P\text{-O-C}$) couplings in two 1,2-oxaphosphol-3-ene P -oxides (0 and 3.7 Hz) [5]. Thus, the absence of ($P\text{...CHPh}$) couplings in **3** and **4** convincingly demonstrates the insertion of sulfur and selenium into the $P\text{-CHPh}$ bond of **1**. Another significant observation is the increase of the 2J ($P\text{...CH}$) coupling between phosphorus and the unsubstituted sp^2 ring carbon from

4.5–7.0 Hz in **1** to 13.9–18.2 Hz in **3** and **4**. The corresponding values in the two 1,2-oxaphosphol-3-ene P -oxides already mentioned are 18.4 and 19.1 Hz [5].

From a mechanistic standpoint, these two insertions can be viewed as [1 + 4] cycloadditions between sulfur and selenium on one side and the phosphadienic isomer **2** on the other side. As far as we know, no such cycloaddition has been reported in the literature until now. Neilson [6] has described the reaction of sulfur with a stable phosphadiene. An initial [1 + 2] cycloadduct, which undergoes ring closure upon partial desulfurization, is obtained:



where $R = \text{SiMe}_3$.

EXPERIMENTAL

All reactions were performed under argon. Nuclear magnetic resonance spectra were recorded on multinuclear WP 80 SY and AC 200 SY Bruker spectrometers operating at 80.13 and 200.13 (^1H), 20.15 and 50.32 (^{13}C), and 32.44 (^{31}P) MHz. Chemical shifts are in parts per million downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and coupling constants are in Hertz. Mass spectra were recorded on a Shimadzu GC-MS QP 1000 instrument at 70 eV under electronic impact. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, France. All the new products gave correct C,H elemental analyses. Silica gel (70–230 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers.

(3-Ethoxy-2,5-diphenyl-2,5-dihydro-1,2-thiaphosphole)pentacarbonyltungsten **3**

Complex **1** (0.3 g, 5×10^{-4} mol) and sulfur **3** (0.04 g, 1.25×10^{-3} mol) were heated for 4 h at 130°C in 10 mL of xylene. After evaporation, the crude residue was chromatographed with pentane- CH_2Cl_2 4:1. Yield of **3**, 150 mg (47%). Results by ^1H NMR (CDCl_3), δ 1.35 (t, 3H, Me), 3.90 (m, 2H, OCH_2), 5.25–5.5 (m, 2H, $\text{CHPh} + =\text{CH}$), 6.8–7.7 (m, 10H, Ph); by IR (CH_2Cl_2), γ (CO) 2070, 1942 cm^{-1} ; by MS (^{184}W), m/z 624 (M^+ , 13%), 484 ($\text{M}-5\text{CO}$, 100%).

(3-Ethoxy-2,5-diphenyl-2,5-dihydro-1,2-selenaphosphole)pentacarbonyltungsten **4**

Complex **1** (0.3 g, 5×10^{-4} mol) and a large excess of selenium were heated 2 h at 120°C in 10 mL of

TABLE 1 Comparative ^{13}C and ^{31}P NMR data for complexes **1**, **3**, and **4**^a

Compound	1	3	4
CHPh δ	46.38 – 45.13	57.16	50.41 – 49.91
$J(\text{C}\dots\text{P})$	31.7 – 30.2	0	0 – 0
$=\text{C}-\text{OEt}$ δ	155.70 – 155.93	160.13 – 159.77	160.53
$J(\text{C}\dots\text{P})$	57.9 – 58.4	57.7 – 56.9	51.7
$=\text{CH}$ δ	107.10 – 105.94	109.52 – 107.83	110.54 – 109.18
$J(\text{C}\dots\text{P})$	4.5 – 7.0	14.4 – 18.2	13.9 – 17.3
$\delta^{31}\text{P}$	57.38 – 61.14	49.25 – 46.16	33.74 – 29.68
	(major) (minor)	(minor) (major)	(major) (minor)

^a δ in ppm, J in Hz; reference standards: internal, Me_4Si for ^{13}C , and external, 85% H_3PO_4 for ^{31}P ; solvent, CDCl_3 .

xylene. After evaporation, the crude residue was chromatographed with pentane– CH_2Cl_2 7 : 3. Yield of **4**, 170 mg (50%). Results by ^1H NMR (CDCl_3), δ 1.41 (2t, 3H, Me), 3.97 (m, 2H, OCH_2), 5.55–5.85 (m, 2H, CHPh + $=\text{CH}$), 7.0–7.76 (m, 10H, Ph); by IR (CH_2Cl_2), γ (CO) 2075, 1945 cm^{-1} ; by MS (^{80}Se , ^{184}W), m/z 672 (M^+ , 13%), 532 ($\text{M}-5\text{CO}$, 100%).

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