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REACTION OF DIPHOSPHENES WITH ELEMENTAL SELENIUM. ISOLATION AND CHARACTERIZATION OF SELENADIPHOSPHIRANES AND DISELENOXOPHOSPHORANE

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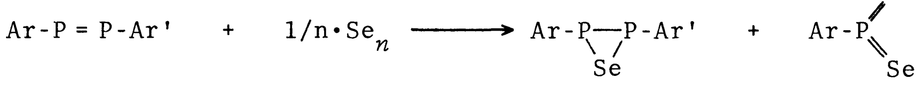
Sterically protected thermally stable 1,2,3-selenadiphosphirane and diselenoxophosphorane were isolated from the reaction of *E*-bis(2,4,6-tri-*t*-butylphenyl)diphosphene with elemental selenium.

Recently, the chemical reactivities and physicochemical properties of diphosphenes have been of current interest because of the presence of an unusual P=P double bond.[1 - 4] We reported the reaction of a diphosphene, *E*-bis(2,4,6-tri-*t*-butylphenyl)diphosphene (**1a**), with sulfur[5] to give the corresponding diphosphene monosulfide, which isomerizes to 1,2,3-thiadiphosphirane. The X-ray structures of each compound have been already determined.[1,5,6]

We now wish to report the reaction of **1** with elemental selenium. The diphosphene **1a** (192 mg, 0.347 mmol) was dissolved in triethylamine (8 ml), then elemental selenium (31.3 mg, 1.14 equiv.) was added and the mixture was stirred in the dark at 70 °C under argon for 2 h. The mixture became dark green instantaneously and then gradually turned pale yellow with some insoluble material, while the solid selenium almost disappeared during the reaction. The reaction mixture was concentrated and the residue was chromatographed over silica gel (hexane - benzene) to give 2,3-bis(2,4,6-tri-*t*-butylphenyl)-1,2,3-selenadiphosphirane (**2a**; 25.7 mg, 17% yield based on the diphosphene **1a**) and diselenoxo(2,4,6-tri-*t*-butylphenyl)phosphorane (**3**; 4% yield).



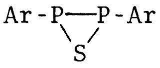
1 **2** **3**

Ar = 2,4,6-$Bu^t_3C_6H_2$
a: Ar' = Ar; **b**: Ar' = 2,4,6-$Me_3C_6H_2$

2a: pale yellow crystals, mp 133.5 °C (decomp); ^{1}H NMR ($CDCl_3$) δ 7.11 (s, 4H, Ar-arom.), 1.54 (s, 36H, o-Bu^t), and 1.25 (s, 18H, p-Bu^t); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P -47.4 (s) ppm from external 85% H_3PO_4 (satellite, d, $^1J_{PSe} = 131.8$ Hz); UV (CH_2Cl_2) λ_{max} (ε) 248 (17900) and 294 nm (9760); HR-MS m/e Found 632.3170 (M^+), Calcd for $C_{36}H_{58}P_2Se$ 632.3177.

3: green crystals, mp 45 - 47 °C (decomp); ^{1}H NMR ($CDCl_3$) δ 7.50 (d, $^4J = 6.4$ Hz, 2H, Ar-arom.), 1.78 (d, $^5J = 0.9$ Hz, 18H, o-Bu^t), and 1.33 (s, 9H, p-Bu^t); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P 273.0 (s) ppm (satellite, d, $^1J_{PSe} = 854.5$ Hz); MS m/e 434 and 436 (the mass spectrum of the parent peaks showed a reasonable pattern for that containing two selenium atoms); UV (cyclohexane) λ_{max} (ε) 260 (9800) and 405 nm (2100).$^{7)}$

Both of the selenium compounds thus obtained are thermally stable at room temperature but quite sensitive to light. They decompose on heating at their melting points or exposing to air and/or light on a TLC plate resulting in unidentified reddish material. The δ_P values of 2a and 3 are similar to those for the corresponding sulfur analogs (4: δ_P -65.1 ppm$^{6)}$ and 5: δ_P 298.2 ppm$^{8,9)}$) respectively.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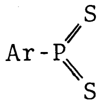
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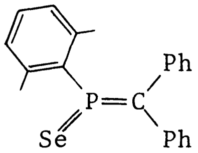
It should be noted that the value of the spin-spin coupling constant between the phosphorus and the selenium, $^1J_{PSe}$, observed for 3 as satellite is quite similarly large to that reported for P-2,5-dimethylphenyl(diphenylmethylene)selenoxophosphorane (6: $J_{PSe} = 890$ Hz) by Bickelhaupt et al.$^{10)}$ and that for N-t-butylimino(t-butyltrimethylsilylamino)selenoxophosphorane (7: $J_{PSe} = 960$ Hz) by Scherer et al.$^{11)}$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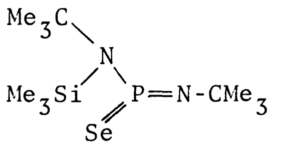
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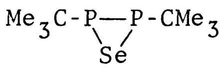
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Very similarly, mesityl-2,4,6-tri-t-butylphenyldiphosphene (1b) was allowed to react with elemental selenium in triethylamine and the formation of the corresponding 1,2,3-selenadiphosphirane (2b) was observed in the ^{31}P NMR spectrum analysis. $^{31}P\{^1H\}$ NMR appeared as an AB pattern centered at -69.2 and -72.0 ppm with the coupling constant $^1J_{PP}$ = 246.6 Hz, the value of which was first directly observed by the present preparation of the unsymmetrical selenadiphosphirane **2b**. However, **2b** was not stable enough to permit isolation by a similar method employed for **2a**. A symmetrical selenadiphosphirane was first described by Baudler et al.,[12] but, the reported 2,3-di-*t*-butyl derivative **8** was quite unstable toward heat (<-30 °C), light, and polar solvents. The present selenadiphosphirane **2a** is stable if strong light is avoided. We have recently prepared the sulfur analog of **2b**, mesityl-2,4,6-tri-*t*-butylphenylthiadiphosphirane (**9**) [δ_P (C_6H_6, AB pattern) -81.9 and -84.0 ppm, $^1J_{PP}$ = 232.9 Hz].[13] On the other hand, Baudler[14] has predicted that in the phosphorus-containing three-membered ring systems (P_2E), an increase in the P-E covalent bond length widens the endocyclic bond angles at the phosphorus atoms causing a chemical shift in the down field direction: at the same time, the absolute value of the $^1J_{PP}$ coupling constant increases. This is also the case for our thia- (**9**) and selenadiphosphiranes (**2b**): both δ_P and $^1J_{PP}$ may be interpreted in the same way by assuming that the bond length of P-Se is longer than that for P-S.

Thus **2a** was allowed to react with tris(dimethylamino)phosphine in toluene in the dark under argon at room temperature for 1 h, the deselenation reaction took place to give the diphosphene **1a** almost quantitatively, in contrast to the results of the corresponding thiadiphosphirane **4** which did not react at all even under severer reaction conditions,[5,6] indicating less steric protection in **2a** than **4**.

$$\mathbf{2a} \quad + \quad \mathrm{P(NMe_2)_3} \longrightarrow \mathbf{1a}$$

$$\mathbf{4} \quad + \quad \mathrm{P(NMe_2)_3} \not\longrightarrow \mathbf{1a}$$

The reaction mechanisms for giving **2** and **3** have been unclear so far. Attempts to isolate the reaction intermediate(s) are under way.

The X-ray crystallographic analysis of **2a** is in progress now at Osaka City University by Dr. Ken Hirotsu.

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