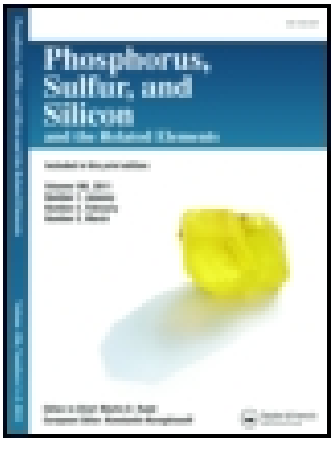

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1,2,4-SELENADIPHOSPHOLES—NOVEL HETEROCYCLIC COMPOUNDS CONTAINING LOW-COORDINATED PHOSPHORUS ATOMS[1]

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1,2,4-SELENADIPHOSPHOLES—NOVEL HETEROCYCLIC COMPOUNDS CONTAINING LOW-COORDINATED PHOSPHORUS ATOMS[1]

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Dedicated to Professor J. G. Verkade on the occasion of his 60th birthday

(Received January 25, 1996; in final form February 27, 1996)

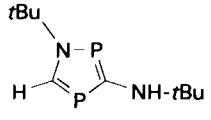
The thermal reactions (at 120°C) of the 1,2,3-selenadiazole **8** with the phosphaalkynes **6a** and **6b** gave rise to the previously unknown title compounds in 17% and 16% yield, respectively. These compounds are formed by a sequence of [3 + 2]-cycloreversion and cycloaddition reactions.

Key words: Low-coordinated phosphorus, 1,2,4-selenadiphospholes, phosphaalkyne selenides, selenoxophosphinidines, phosphaalkynes.

INTRODUCTION

Heterophospholes play a major role in the development of the chemistry of low-coordinated phosphorus. Condensation reactions[2,3] and [3 + 2]-cycloaddition processes, in particular with phosphaalkynes,[4,5] have provided accesses to a wide range of phospholes containing one or more additional heteroatoms in the ring.

In this short paper, we report on the discovery of a previously unknown class of compounds, the 1,2,4-selenadiphospholes **3**.



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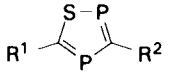

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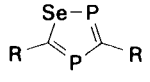
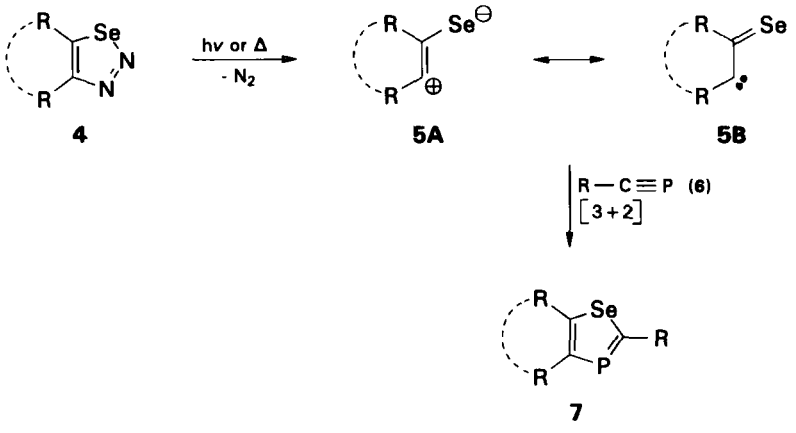
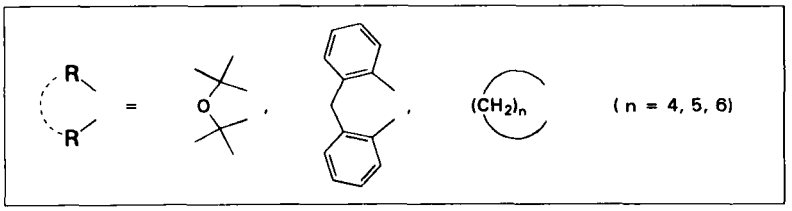


3

A 1,2,4-azadiphosphole **1** had been obtained previously by the spontaneous dimerization of *tert*-butylaminophosphaacetylene.[6] Furthermore, some 1,2,4-thiadiphospholes **2** carrying both identical and different C-substituents at the 3 and 5 positions have been prepared in the last ten years.[7–11]

The starting point for our investigations in this field was the [3 + 2]-cycloaddition of the selenoxocarbenes **5A** ⇔ **5B** (or the respective 1,3-diradicals) to phosphaalkynes **6**.[12]



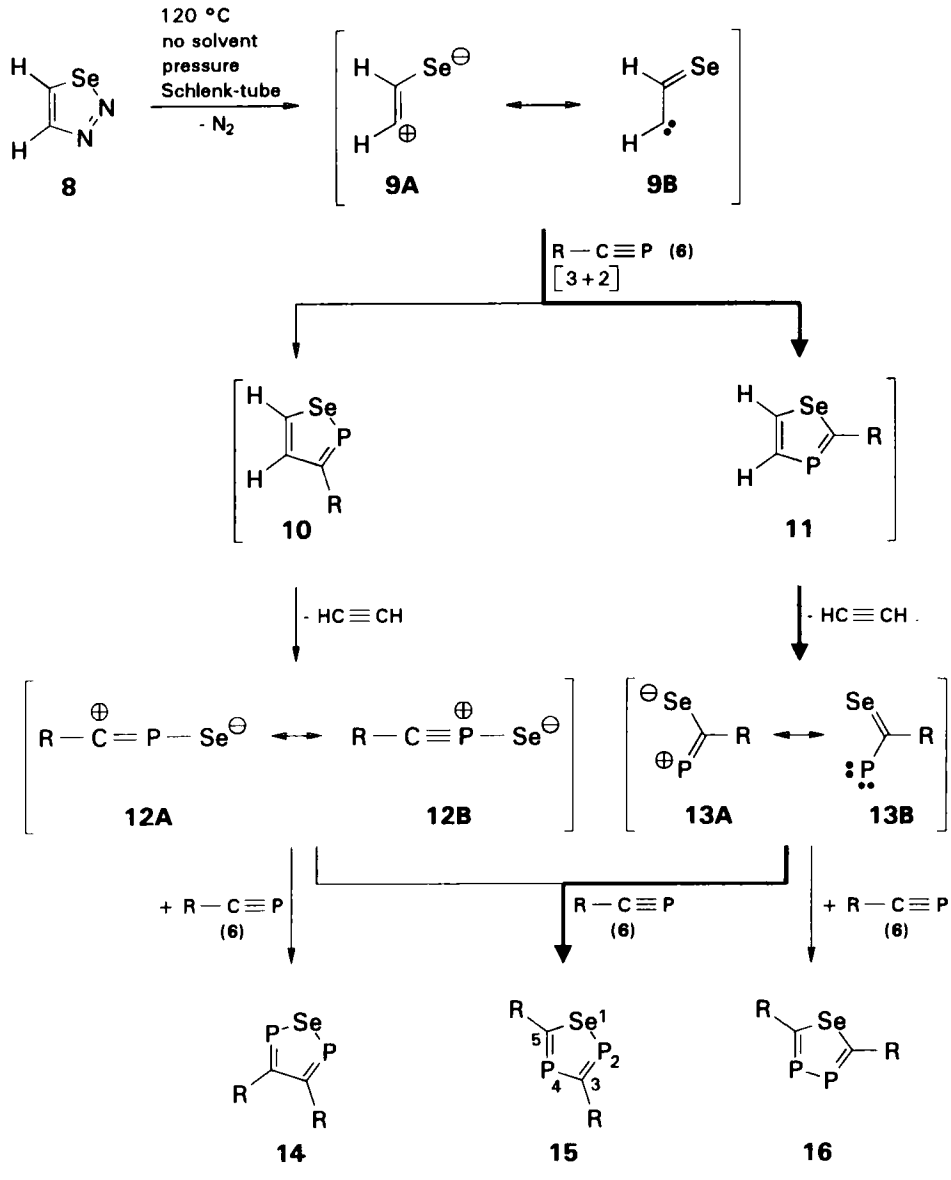


The dipoles were generated photolytically or thermally from the 1,2,3-selenadiazoles **4** by cleavage of nitrogen and then underwent regiospecific cycloaddition reactions with the P/C triple bonds of **6** to furnish the 1,3-selenaphospholes **7**.[12] However, when we subjected the parent, unsubstituted 1,2,3-selenadiazole **8** to reaction with the phosphaalkynes **6** under comparable conditions, we were confronted with the unexpected and unforeseeable formation of the title compounds **15a** and **b**.

RESULTS

The reactions of **8** with a threefold excess of **6a** or **b** were performed in the absence of a solvent and, after column chromatographic work-up on silica gel, furnished the 1,2,4-selenadiphospholes **15a** and **b** in the form of pale yellow oils. The compositions of the products were established by elemental analysis and mass spectroscopy. Volumetric determination of the amount of gas liberated during the reactions revealed that, in addition to nitrogen, a second equivalent of a gaseous compound (in these cases, acetylene) was released during the reactions. Nevertheless, the yields of the product isolated were unexpectedly low.

The structures of the 1,2,4-selenadiphospholes **15a** and **b** are unequivocally substantiated by the NMR spectroscopic data; this will be shown below for example of the di-*tert*-butyl derivative **15a**. In the ^{77}Se NMR spectrum, the heteroatom gives rise to a double doublet signal at $\delta = 723.0$ with a $^{1}J_{Se,P}$ coupling constant of 501.7 Hz. This J value is in good agreement with those of other compounds containing a comparable structural unit.[13,14] The $^{2}J_{Se,P}$ value of 62.3 Hz is also of the expected magnitude.[14] In the ^{31}P NMR spectrum the $\lambda^3\sigma^2$-phosphorus nuclei give rise to signals at very low field,[13] namely $\delta = 291.2$ (P-2) and 260.4 (P-4). Both signals are split



6, 10 - 16	a	b
R	*t*Bu	*t*Pent

into doublets by selenium (see above) and/or by phosphorus ($^2J_{P,P}$ = 49.2), respectively. Thus, the formation of isomers such as **14a,b** or **16a,b** can be excluded.

Finally, the ^{13}C NMR spectrum of **15a** confirmed the sequence of atoms deduced above. The splitting of the signal for C-3 into a double doublet (δ = 222.0) with $^1J_{C,P}$ couplings of 82.2 and 60.4 Hz as well as that of the C-5 signal (δ = 215.6)

with $^1J_{C,P}$ = 67.2 Hz and $^2J_{C,P}$ = 6.1 Hz are in complete harmony with the proposed structure. The remaining ^{13}C NMR data are directly related to the structure and are given in the experimental section.

It can safely be assumed that, in the primary step of the thermal reaction, the selenadiazole **8** decomposes to nitrogen and the selenoxocarbene **9A** ⇔ **9B**; this is followed by the [3 + 2]-cycloaddition of the sextet dipole to the first equivalent of the phosphaalkyne **6** furnishing the 1,3-selenaphosphole **11**. Evidence in support of the intermediate formation of **11** is provided by a ^{31}P NMR spectrum of the mixture of **8** + **6a** recorded after a reaction time of 1 h: in addition to the phosphorus signals of **15a**, this spectrum also contains a signal at δ = 206.6 which is in the same region as the signals of previously known compounds of this type (such as, e.g. **7**).[12] The thermal fragmentation of **11** into acetylene and the selenoxophosphinidine **13A** ⇔ **13B** is followed by the 1,3-dipolar cycloaddition of the latter species to the second equivalent of the phosphalkyne **6** which furnishes the 1,2,4-selenadiphosphole **15**. Of course, it cannot be excluded that the reaction sequence **9** + **6** → **10** → **12** (+**6**) → **15** may also, to a minor extent, contribute to the formation of the product. The [3 + 2]-cycloaddition of the thiobenzoylphosphinidine (**13**, R = Ph, S in place of Se), which was generated by a completely independent route, with phenylphosphaacetylene (**6**, R = Ph) has been reported.[8,9]

EXPERIMENTAL

The reactions were carried out in an argon (purity: ≥99.998%) atmosphere in previously evacuated and baked-out Schlenk pressure tubes. The bulb-to-bulb distillations were performed with a Büchi 6KR50 apparatus, the temperatures given are oven temperatures. Microanalyses were determined using a Perkin Elmer 240 apparatus. The ^1H NMR spectra were obtained on a Varian 390 (90 MHz) spectrometer with TMS as internal standard, the ^{13}C NMR spectra on a Bruker AMX 400 (100.67 MHz) spectrometer with TMS as internal standard, the ^{31}P NMR spectra on a Bruker WP 200 (80.8 MHz) spectrometer with 85% H_3PO_4 as external standard, and the ^{77}Se NMR spectra on a Bruker AMX 400 (76.36 MHz) spectrometer with $Se(CH_3)_2$ as external standard. The mass spectra were recorded on a Finnigan MAT 90 spectrometer.

3,5-Di-tert-butyl-1,2,4-selenadiphosphole (**15a**). 1,2,3-Selenadiazole (**8**; 0.80 g, 6.00 mmol) and *tert*-butylphosphaacetylene[15] (**6a**; 2.38 ml, 18.2 mmol, threefold excess) were heated at 120°C for 5 h in a Schlenk pressure tube. After cooling of the reaction mixture to 25°C, the evolution of two equivalents of nitrogen plus acetylene can be determined by gas volumetric analysis. After separation of the excess phosphaalkyne at 30°C/10^{-3} mbar, the residue was taken up in *n*-hexane/diethyl ether (1:1) and subjected to column chromatography on silica gel (0.063–0.2 mm) with 700 ml of the same solvent mixture. After elution of polymeric components, a pale yellow fraction was obtained which, apart from **15a**, did not contain any other phosphorus-containing compounds (^{31}P NMR monitoring). Similarly, the subsequent fractions also did not contain any phosphorus compounds. After evaporation of the eluted fraction at 30°C/10^{-3} mbar and bulb-to-bulb distillation of the residue at 150°C/10^{-3} mbar, 0.29 g (17%) of product **15a** were obtained as a pale yellow oil. Found (%): C 42.9, H 6.4; calcd. for $C_{10}H_{18}P_2Se$ (%): C 43.0, H 6.5. ^1H NMR ($CDCl_3$): δ = 1.70 d (9H, 5-*t*-Bu, $^4J_{H,P}$ = 1.8 Hz), 1.73 dd (9H, 3-*t*-Bu, $^4J_{H,P}$ = 0.7 and 2.6 Hz, respectively). ^{13}C NMR ($CDCl_3$): δ = 35.5 dd [3-C($\underline{C}H_3$)$_3$, $^3J_{C,P}$ = 1.7 and 9.7 Hz, respectively], 35.8 d [5-C($\underline{C}H_3$)$_3$, $^3J_{C,P}$ = 11.8 Hz], 42.9 pseudo-t [3-$\underline{C}$(CH_3)$_3$, $^2J_{C,P-2}$ = $^2J_{C,P-4}$ = 19.8 Hz], 43.4 dd [5-$\underline{C}$(CH_3)$_3$, $^2J_{C,P}$ = 16.7 Hz, $^3J_{C,P}$ = 6.3 Hz], 215.6 dd (C-5, $^1J_{C,P}$ = 67.2 Hz, $^2J_{C,P}$ = 6.1 Hz), 222.0 dd (C-3, $^1J_{C,P}$ = 82.2 Hz, $^1J_{C,P}$ = 60.4 Hz). ^{31}P NMR ($CDCl_3$): δ = 260.4 d (P-4, $^2J_{P,P}$ = 49.2 Hz), 291.2 dd (P-2, $^2J_{P,P}$ = 49.2 Hz, $^1J_{P,Se}$ = 441 Hz). ^{77}Se NMR ($CDCl_3$): δ = 773.0 dd (Se-1, $^1J_{Se,P}$ = 501.7 Hz, $^2J_{Se,P}$ = 62.3 Hz). MS (70 eV): m/z = 279.8 (61%, M^+).

3,5-Di-tert-pentyl-1,2,4-selenadiphosphole (**15b**). In analogy to the above procedure starting from 1,2,3-selenadiazole (**8**, 0.80 g, 6.00 mmol) and *tert*-pentylphosphaacetylene[16] (**6b**; 7.1 g, 17.5 mmol, as a 45% solution in hexamethyldisiloxane) 0.29 g (16%) of product **15b** were obtained as a pale yellow oil. Found (%): C 46.9, H 7.3; calcd. for $C_{12}H_{22}P_2Se$ (%): C 46.8, H 7.2. ^1H NMR ($CDCl_3$): δ = 0.75, 0.80 each t (each 3H, CH_2—C$\underline{H}_3$, $^3J_{H,H}$ = 7.5 Hz), 1.50 d [6H, 5-C(C$\underline{H}_3$)$_2$, $^4J_{H,P}$ = 2.0 Hz], 1.55 dd [6H,

3-C($\underline{C}H_3$)$_2$, $^4J_{H,P}$ = 0.5 and 2.7 Hz, respectively], 1.85, 1.95 each q (each 2H, $C\underline{H}_2$—CH_3, $^3J_{H,H}$ = 7.5 Hz).[13]C NMR ($CDCl_3$): δ = 9.5 (CH_2—$\underline{C}H_3$), 32.7 dd [3-C($\underline{C}H_3$)$_2$, $^3J_{C,P}$ = 9.2 and 14.3 Hz, respectively], 33.0 d [5-C($\underline{C}H_3$)$_2$, $^3J_{C,P}$ = 13.1 Hz], 40.6 pseudo-t [3-C—$\underline{C}H_2$—CH_3, $^3J_{C,P-2}$ = $^3J_{C,P-4}$ = 8.3 Hz], 40.9 d [5-C—$\underline{C}H_2$—CH_3, $^3J_{C,P}$ = 6.8 Hz], 46.5 pseudo-t [3-C($\underline{C}H_3$)$_2$, $^2J_{C,P-2}$ = $^2J_{C,P-4}$ = 18.6 Hz], 46.7 dd [5-$\underline{C}$(CH_3)$_2C_2H_5$, $^2J_{C,P}$ = 17.5 Hz, $^3J_{C,P}$ = 7.0 Hz], 214.1 dd (C-5, $^1J_{C,P}$ = 73.4 Hz, $^2J_{C,P}$ = 5.9 Hz), 220.4 d (C-3, $^1J_{C,P}$ = 72.7 and 80.5 Hz, respectively). ^{31}P NMR ($CDCl_3$): δ = 261.0 d (P-4, $^2J_{P,P}$ = 48.1 Hz), 295.6 dd (P-2, $^2J_{P,P}$ = 48.1 Hz, $^1J_{P,Se}$ = 439.5 Hz). ^{77}Se NMR ($CDCl_3$): δ = 723.0 dd ($^1J_{Se,P}$ = 439.5 Hz, $^2J_{Se,P}$ = 62.3 Hz). MS (70 eV): m/z = 293.8 (70%, M^+).

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REFERENCES

1. Organophosphorus Compounds 113; for part 112, see: B. Breit and M. Regitz, *Chem. Ber.*, **129** (1996), in press.
2. A. Schmidpeter and K. Karaghiosoff, in "Multiple Bonds and Low Coordination in Phosphorus Chemistry," M. Regitz and O. J. Scherer, eds., Thieme, Stuttgart, 1990, p. 258 ff.
3. R. K. Bansal, K. Karaghiosoff, N. Gandhi and A. Schmidpeter, *Synthesis*, 361 (1995).
4. M. Regitz, in "Multiple Bonds and Low Coordination in Phosphorus Chemistry," M. Regitz and O. J. Scherer, eds., Thieme, Stuttgart, 1990, p. 58 ff.
5. M. Regitz, *Chem. Rev.*, **90,** 191 (1990).
6. A. S. Ionkin, S. N. Ignat'eva, I. A. Litvinov, V. A. Naumov and B. A. Arbusov, *Heteroatom Chemistry*, **2,** 577 (1991).
7. R. Appel and R. Moors, *Angew. Chem.*, **98,** 570 (1986); *Angew. Chem., Int. Ed. Engl.*, **25,** 567 (1986).
8. G. Märkl and W. Hölzl, *Tetrahedron Lett.*, **30,** 4501 (1989).
9. G. Märkl, W. Hölzl, A. Kallmünzer, M. L. Ziegler and B. Nuber, *Tetrahedron Lett.*, **33,** 4421 (1992).
10. E. Lindner, C. Haase, H. A. Mayer, M. Kemmler, R. Fawzi and M. Steinmann, *Angew. Chem.*, **105,** 1521 (1993); *Angew. Chem., Int. Ed. Engl.*, **32,** 1424 (1993).
11. E. Lindner, T. Schlenker and C. Haase, *J. Organomet. Chem.*, **464,** C31 (1994).
12. B. Burkhart, S. Krill, Y. Okano, W. Ando and M. Regitz, *Synlett.* 356 (1991).
13. K. Karaghiosoff and A. Schmidpeter, *Phosphorus and Sulfur*, **36,** 217 (1988).
14. L. Quin, "^{31}P-NMR Spectroscopy," Wiley, New York, 1988.
15. G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch.*, **36b,** 16 (1981). Optimized procedure: W. Rösch, U. Hees and M. Regitz, *Chem. Ber.*, **120,** 1645 (1987).
16. T. Allspach, Dissertation, University of Kaiserslautern, 1986.