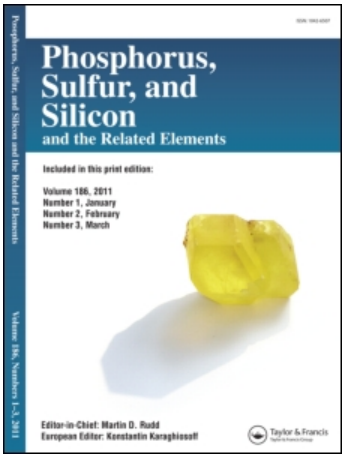


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SUBSTITUTED 4,5-DIOXO-1,3-DIAZA-2λ³,4λ⁴-DIPHOSPHOLANE AND RELATED COMPOUNDS

Chen Ru-yu[a]; Cheng Leifeng[a]
[a] Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, China

To cite this Article Ru-yu, Chen and Leifeng, Cheng(1989) 'SUBSTITUTED 4,5-DIOXO-1,3-DIAZA-2λ³,4λ⁴-DIPHOSPHOLANE AND RELATED COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 44: 3, 193 — 195
To link to this Article: DOI: 10.1080/10426508908040608
URL: http://dx.doi.org/10.1080/10426508908040608

Phosphorus, Sulfur, and Silicon, 1989, Vol. 44, pp. 193–195
Reprints available directly from the publisher
Printed in the United Kingdom

SUBSTITUTED 4,5-DIOXO-1,3-DIAZA-2λ³,4λ⁴-DIPHOSPHOLANE AND RELATED COMPOUNDS

CHEN RU-YU* and CHENG LEIFENG

(Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, China)

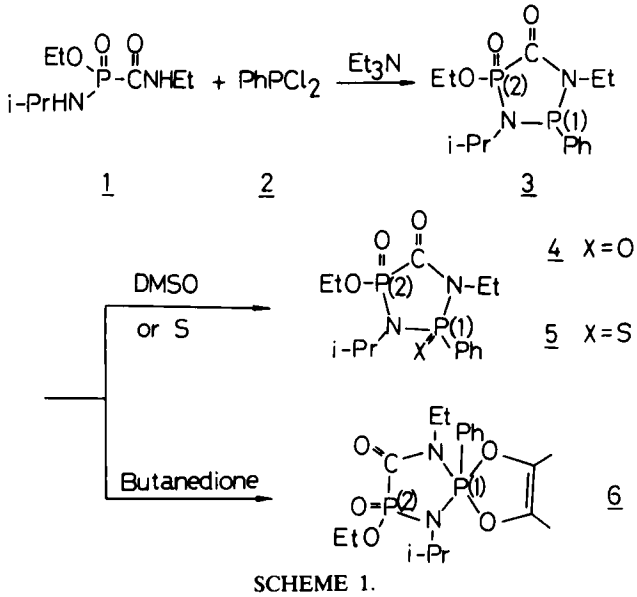
(Received October 18, 1988)

Cyclization of **1** with **2** yielded the title compound **3**, which was transformed into the corresponding 1,3,2,4-diazadiphospholanes **4** and **5** by using DMSO or sulfur respectively. The addition reaction of **3** with butanedione gave 3,4-di-oxo-1-phenyl-2,5-diaza-6,9-dioxa-1λ⁵,3λ⁴-diphosphaspiro[4,4]nonane **6**. The structures of **3**, **4** and **5** were confirmed by elemental analysis, IR, NMR and GC–MS. Although **6** could not be isolated in pure form because of its rapid decomposition, the ^{31}P NMR data indicated its existence. It was found that there were cis- and trans-isomers in **3**, **4**, **5** and **6**.

Key words: 1,3,2,4-Diazadiphospholane; synthesis; cyclization; oxidation; coordinate number; isomer.

Recently, many interesting diphosphorus heterocyclic compounds were reported in the literature encouraging our attempt to synthesize compounds which contain two phosphorus atoms with different coordination number, such as the title compounds **4**, **5** and **6**.

1,3-Diaza-2λ³,4λ⁴-diphospholane **3** was prepared through the cyclization of ethyl *N*-isopropyl-ethylcarbamoylphosphonamidate **1** with phenyl dichlorophosphine **2** in the presence of triethylamine. The tricoordinated phosphorus atom in **3** could be transformed into the phosphorus oxide **4** by oxidation with DMSO or into the phosphorus sufilde **5** by sulfurization. The condensation of **3** with butanedione yielded the pentacoordinated phosphorus compound **6** (Scheme 1).



SCHEME 1.

RESULTS

There exist a cis-isomer with substituents at the two phosphorus atoms located at the same side of the five-membered ring and a trans-isomer with substituents located at different sides for the compounds **3**, **4**, **5** and **6**. In the ^{31}P NMR spectra the two isomers had different chemical shifts and coupling constants. In the previous work[1,2] it had been reported that two isomers of the derivatives of **5** were separated by HPLC and examined by ^{31}P NMR and X-ray diffration indicating that in ^{31}P NMR spectra the cis-isomer appeared at upfield and had a larger coupling constant J_{P_1,P_2} than the trans-isomer. The fact that the cis-isomer had a larger coupling constant $J_{P_1P_2}$ is consistent with its better planarity of the five-membered ring. It is believed that compounds **3**, **4**, **5** and **6** have structures similar to those described previously.[1,2] Thus, they have similar ^{31}P NMR spectra, i.e. cis-isomers appear at upfield with larger coupling constants $J_{P_1P_2}$ and the trans-isomers at downfield with smaller $J_{P_1P_2}$ (Table I).

TABLE I

^{31}P NMR data of compounds **3**, **4**, **5** and **6** (δ in ppm, J in Hz)

	δ_P					
	P_1		P_2		$J_{P_1P_2}$	
Compound	trans	cis	trans	cis	trans	cis
3	79.90	78.21	−1.10	−1.16	24.41	29.30
4	11.79	11.35	−1.94	−2.53	21.97	24.41
5	64.33	63.26	−2.54	−3.07	16.12	17.59
6	−43.30	−44.18	−2.76	−3.11	27.14	36.55

The compound **6** could not be isolated in pure form because of rapid decomposition, but its ^{31}P NMR data indicated that it is pentacoordinate in solution. The conversion of **3** into pentacoordinated **6** is very slow. The ^{31}P NMR showed no significant conversion after standing 30 min. at room temperature and about 25% yield (estimated from the signals) after 24 hours. After even a longer time, no change was observed.

The existence of cis- and trans-isomers of **4** and **5** was also confirmed by GC-MS. The 70 eV mass spectra gave molecular ions of cis- and trans-isomers in the case of **4** and **5**. The ^{31}P NMR spectra of the different fractions indicated that the retention time was 7.156 min. ($M^+ = 344$, 27%) for cis-**4**, 7.025 min. ($M^+ = 344$,26%) for trans-**4**; 7.997 min. ($M^+ = 360$, 9%) for cis-**5** and 7.769 min. ($M^+ = 360$,15%) for trans-**5**. Also, the 70 eV mass spectra gave the molecular ion of **3** ($M^+ = 328$, 17%).

EXPERIMENTAL

IR spectra were recorded on NICOLET 5DX instrument. NMR spectra were recorded on JEOL FX-90Q instrument at 90 MHz(^1H, TMS) and 36.19 MHz (^{31}P, ext. 85% H_3PO_4). GC-MS were obtained at 70 eV with chromatographic column of Ultra 2 (crosslinked 5% Ph Me Silicon, 25 m × 0.2 mm × 0.33 μm film thickness) on HP 5988A instrument. Elemental analysis were done with YANACO CHN CORDER MT-3 instrument. The preparation of **1** was reported previously.[3] Compound **2** was prepared according to literature methods.[4]

1-Ethyl-2-phenyl-3-isopropyl-4-ethoxy-1,3-diaza-2λ³,4λ⁴-diphospholane (**3**). To a stirred solution of 2.22g (10.0 mmol) of Ethyl N-isopropyl-ethylcarbamoylphosphonamidate (**1**), 2.22 g (22.0 mmol) triethylamine in 30 ml ether and 5 ml anhydrous benzene at −10°C was added dropwise over 20 min. a solution of 1.97 g (11.0 mmol) of phenyl dichlorophosphine (**2**) in 5 ml ether. The reaction mixture was stirred for 2 hrs. at −10°C and then it was warmed to room temperature. TLC (GF_{254}, Silica gel, 150 × 80 × 0.3 mm plat, developing agent: petroleum ether/ethyl acetate (1:1) mixture, UV radiation, at 25°C) indicated the completion of the reaction. The precipitated triethylamine hydrochloride was removed by filtration. After removal of solvent the oily residue was purified through rapid chromatographic technique[5]. Elution with petroleum ether/ethyl acetate(1:1) mixture gave the fraction of Rf = 0.33. By stripping off the solvent under reduced pressure 1.64 g of **3** (colorless vicous liquid) was obtained, yield: 50%. $C_{14}H_{22}N_2O_3P_2$ (Calcd: C, 51.22; H, 6.75; N, 8.53. Found: C, 51.25; H, 6.83; N, 8.59). ν_{max} 1645 (C═O), 1255 (P═O) cm^{-1}. δ_H 0.96 (3H, t, NCH_2CH_3), 1.06 (3H, d, $^1CH_3$), 1.34 (3H, t, OCH_2CH_3), 1.44 (3H, d^2, $^2CH_3$), 3.30 (2H, m, NCH_2), 3.72 (1H, m, CH), 4.26 (2H, m, OCH_2), 7.50 (5H, m, C_6H_5) ppm.

1-Ethyl-2-phenyl-3-isopropyl-4-ethoxy-2,4,5-trioxo-1,3,2,4-diazadiphospholane (**4**). The oily residue of **3** obtained above was dissolved in 10 ml dichloromethane, then 1.56 g (20.0 mmol) of dimethyl sulphoxide was added. The reaction mixture was stirred for 4 hrs. in an oil bath at 50°C, and then it was cooled to room temperature. Solvent were removed and the residue was purified by rapid chromatographic technique (same conditions as above). The yield of **4** (Rf = 0.28, colorless viscous liquid) was 1.31 g (38%). $C_{14}H_{22}N_2O_4P_2$ (Calcd: C, 48.84; H, 6.44; N, 8.14. Found: C, 48.79; H, 6.37; N, 8.09). ν_{max} 1655 (C═O), 1250, 1220 (P═O) cm^{-1}. δ_H 0.90 (3H, t, NCH_2CH_3), 1.28 (9H, m, $3CH_3$), 3.12 (2H, m, NCH_2), 3.76 (1H, m, CH), 4.32 (2H, m, OCH_2), 7.56 (5H, m, C_6H_5) ppm.

1-Ethyl-2-phenyl-3-isopropyl-4-ethoxy-4,5-dioxo-2-thio-1,3,2,4-diazadiphospholane (**5**). The oily residue of **3** obtained above was dissolved in 15 ml anhydrous benzene, 0.35 g (11.0 mmol) sulfur powder was added and the reaction mixture was refluxed for 10 hrs. After removal of the solvent the residue was dissolved in acetone to precipitate the unreacted sulfur, which was removed by filtration. Acetone was stripped off under reduced pressure and the residue was purefied by rapid chromatographic technique (same conditions as above). The yield of **5** (Rf = 0.39) was 1.92g(53%, m.p. 94–96°C). $C_{14}H_{22}N_2O_3P_2S$(Calcd: C, 46.66; H, 6.15; N, 7.77. Found: C, 46.81; H, 6.25; N, 7.66). ν_{max} 1680 (C═O), 1250 (P═O), 578 (P═S) cm^{-1}. δ_H 0.92 (3H, t, NCH_2CH_3), 1.20 (3H, d, $^1CH_3$), 1.35 (3H, t, OCH_2CH_3), 1.42 (3H, d, $^2CH_3$), 3.32 (2H, m, NCH_2), 3.68 (1H, m, CH), 4.34 (2H, m, OCH_2), 7.50, 7.92 (5H, m, C_6H_5) ppm.

1-Phenyl-2-isopropyl-3-ethoxy-5-ethyl-7,8-dimethyl-3,4-dioxo-2,5-diaza-6,9-dioxa-1λ⁵,3λ⁴-diphospha-spiro[4,4]nonane-8-ene (**6**). Butanedione (0.2 g, 2.3 mol) was added with a syringe to a solution of **3** (0.5 g, 1.5 mol) in 2 ml of anhydrous CD_3CN which was kept in a septum stoppered NMR sample tube in nitrogen atmosphere. After 24 hrs., ^{31}P NMR was taken indicating about 25% yield of the desired product (Table I).

REFERENCES

1. Wang Honggen, Wang Ruji, Yao Xinkan, Cheng Leifeng and Chen Ruyu, *J. Struct. Chem.*, **6**, 139 (1987).
2. Cheng Leifeng, Chen Ruyu, Wang Ruji and Wang Honggen, *ibid.*, **7**, 70 (1988).
3. Chen Ruyu, Cheng Leifeng, *Chemical Journal of Chinese Universities*, in press.
4. B. Buchner, *Org. Syn.*, **31**, 88 (1951).
5. W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).