Heteroatom Chemistry
Volume 10, Number 2, 1999

Cycloaddition of CO_2 and CS_2 to a Cyclic Phosphazene

Thomas von Criegern,[1] Kurt Polborn,[1] and Alfred Schmidpeter[2]

[1]*Institut für Anorganische Chemie der Ludwig-Maximilians-Universität, Meiserstrasse 1, München, Germany*

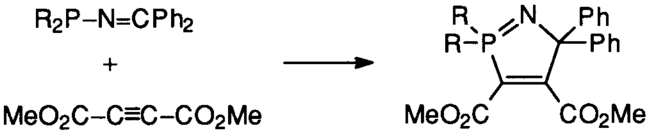
[2]*Institut für Organische Chemie der Ludwig-Maximilians-Universität, Karlstrasse 23, D-80333 München, Germany*

Received 30 July 1998; revised 8 September 1998

ABSTRACT: *Carbon dioxide and carbon disulfide give crystalline cycloadducts with the phosphazene bond of a 1,2λ^5-azaphosphole. The CO_2-adduct fully dissociates in solution, the CS_2-adduct on short heating only to a small part. On longer heating, the latter rearranges in two successive 1,3-shifts to give a thiophosphinylimino dihydrothiophene, the structure of which is revealed by X-ray analysis.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:167–170, 1999

INTRODUCTION

The 1,2λ^5-azaphospholes **1** are easily accessible from the cycloaddition of methyl acetylene dicarboxylate and diphenylmethylene aminophosphines [1]; δ^{31}P = 55.1 (**1a**), 47.4 (**1b**).

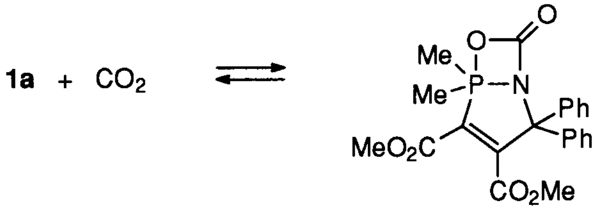


1a, R = Me
1b, R = Ph

They are examples of phosphazenes (iminophosphoranes) that deviate, however, significantly in reactivity from the usual. As part of a five-membered ring, the phosphazene unit becomes much more prone to addition and cycloaddition reactions than in open chain or larger ring compounds. A number of various [2 + 2] and [3 + 2] cycloaddition reactions have been shown with compounds **1** [2–9], among them the cycloaddition of heterocumulenes such as isocyanates [3], isothiocyanates [4], and diphenyl ketene [5]. The cycloaddition of CS_2 has once been mentioned [9]. Here we report about the addition of carbon dioxide and carbon disulfide and also about the rearrangement of a cycloadduct of the latter.

ADDITION OF CO_2

A solution of the yellow compound **1a** absorbs carbon dioxide if the resulting cycloadduct at the same time is made to precipitate. The crystalline and colorless adduct **2** is stable at room temperature and has been identified by elemental analysis and IR spectrum.



2

In solution, it redissociates, however, establishing a mobile equilibrium from which the carbon dioxide

---

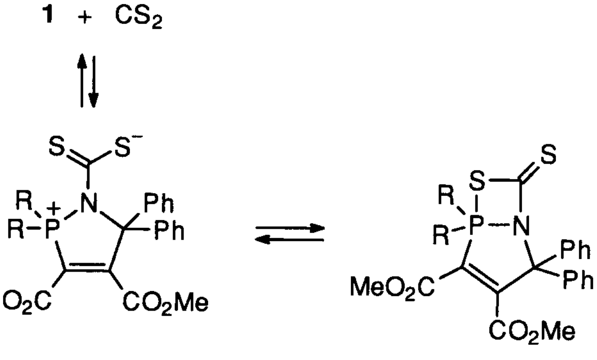
Correspondence to: Alfred Schmidpeter

CCC 1042-7163/99/020167-04

is lost. The room temperature ^{31}P NMR spectra consequently only show broad signals with the chemical shift varying around $\delta^{31}P = 20$, which can be understood as averaged shifts of **2** and **1a.** No reaction of carbon dioxide could be observed with **1b.**

ADDITION OF CS$_2$

Carbon disulfide and the azaphospholes **1a,b** react to yield crystalline yellow adducts **4.** The high field chemical shift of their chloroform solution $\delta^{31}P = -40.0$ (**4a**), -38.3 (**4b**) clearly indicates the pentacoordination of phosphorus. As for other phosphoranes, with the phosphorus atom at the bridgehead of a bicyclo[3.2.0]heptane skeleton, a trigonal bipyramidal structure with the rings in meridional placement [10,11] must be expected. This structure is verified for **4a** by the equivalence of the two *P*-methyl groups in the ^{1}H NMR spectrum.



3 **4**

For a DMSO solution of **4a,** $\delta^{31}P = 25.9$ was found, indicating a mobile equilibrium with the ring-opened zwitterionic form and suggesting a 15–20 % contribution of **3a** in the polar solvent. Heating the anisole solution of **4a,b** for a short time to 100°C, on the other hand, results in ^{31}P NMR spectra that show both the signals of **4** and **1**. When the solutions are cooled, the relative intensity of the latter signal decreases again. This indicates a relatively slow and reversible thermal dissociation of **4.**

THERMAL REARRANGEMENT

Heating the anisole solutions of **4a,b** for longer times (1 h) to 130–150°C results in new products with $\delta^{31}P = 62.0$ (**6a**), 53.1 (**6b**), which accordingly contain a tetracoordinate phosphorus atom. Compound **6b** has been isolated as bright yellow crystals. It has the same composition as **4b** and consequently originates from a rearrangement of **4b**. ^{31}P NMR and MS hint at the presence of a Ph$_2$PS group; the full structure, however, becomes evident only from the X-ray structure analysis (Figure 1, Table 1).

In the rearrangement, three σ bonds (CS, CP, and CN) must be broken, and two bonds (CC and CS) must be formed. This necessitates at least one intermediate. As **4** is a Wittig-type adduct, its most obvious reaction would be the cycloreversion of the four-membered ring with the phosphorus atom becoming four coordinate and the nitrogen atom being inte-

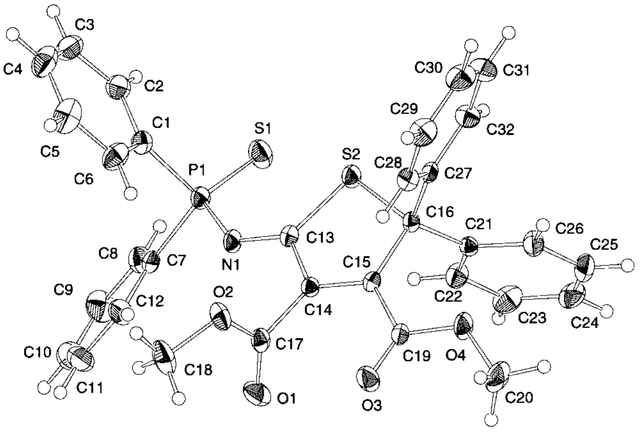
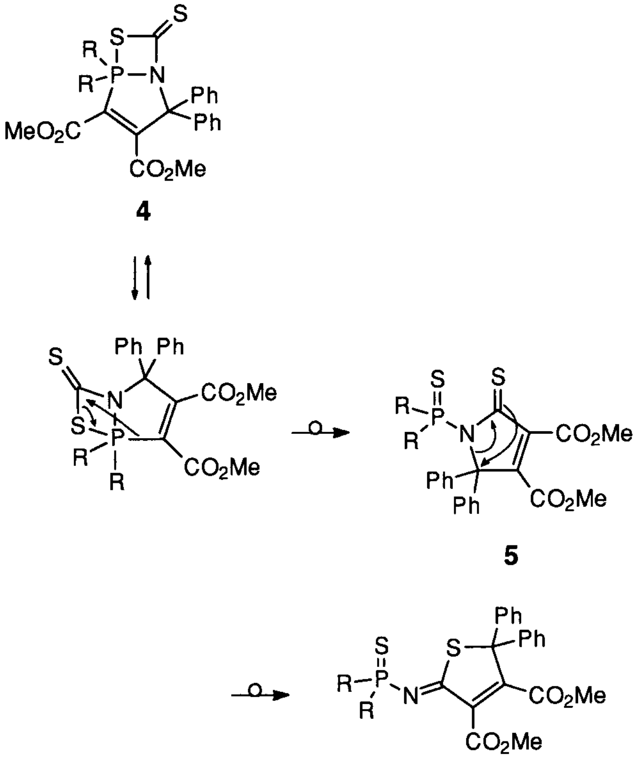


FIGURE 1 Molecular structure of **6b** in the crystal (thermal ellipsoids with 30% probability).

TABLE 1 Relevant Bond Lengths [Å] and Angles [°] for **6b**

S1-P1	1.940(1)	C13-S2-C16	94.1(1)
S2-C13	1.753(2)	N1-P1-C7	100.4(1)
S2-C16	1.879(2)	N1-P1-C1	103.7(1)
P1-N1	1.677(2)	C7-P1-C1	104.8(1)
P1-C7	1.810(2)	N1-P1-S1	118.2(1)
P1-C1	1.811(3)	C7-P1-S1	113.0(1)
O1-C17	1.189(3)	C1-P1-S1	114.9(1)
O2-C17	1.322(3)	N1-C13-C14	119.0(2)
O3-C19	1.190(3)	N1-C13-S2	131.3(2)
O4-C19	1.317(3)	C14-C13-S2	109.7(2)
N1-C13	1.277(3)	C15-C14-C13	115.7(2)
C13-C14	1.474(3)	C15-C14-C17	128.2(2)
C14-C15	1.334(3)	C13-C14-C17	116.0(2)
C14-C17	1.505(3)	C14-C15-C19	120.0(2)
C15-C19	1.499(3)	C14-C15-C16	116.7(2)
C15-C16	1.524(3)	C19-C15-C16	123.3(2)
		C15-C16-C27	113.5(2)
		C15-C16-C21	109.7(2)
		C27-C16-C21	115.1(2)
		C15-C16-S2	103.6(1)
		C27-C16-S2	105.8(2)
		C21-C16-S2	108.3(2)
		O1-C17-O2	126.9(2)
		O1-C17-C14	124.6(2)
		O2-C17-C14	108.4(2)
		O3-C19-O4	124.8(2)
		O3-C19-C15	123.0(2)
		O4-C19-C15	112.2(2)

grated in an isothiocyanate group. As the PN bond is kept in **6**, it must not open in this reaction, however. Instead, after pseudorotation of **4** to its facial isomer, the opening of the CS bond is accompanied by the opening of the CP bond and the closure of the CC bond. This leads to compound **5** as an intermediate on the way from **4** to **6**, and there seems no reasonable alternative to it.



4

5

6

For the rearrangement from **5** to **6**, a two-step pathway seems most likely: At first, the CN bond opens to give a zwitterion that in forming the CS bond closes the ring again [12]. The result is in accord with an aza-Wittig reaction inasmuch as from the P=N bond of **1** and a C=S bond of the carbon disulfide the P=S and the C=N bond of **6** are formed.

EXPERIMENTAL

IR: Perkin-Elmer 325, nujol/hostaflon mull. NMR: Varian HR 100, TMS internal, H_3PO_4 external. MS: Varian CH 7. Compounds **1** were prepared as described [1].

CO_2-Adduct 2

To a yellow solution of **1a** (1.55 g, 5.04 mmol) in 3 mL of chloroform, *n*-pentane was carefully added to gain supersaturation. When dry carbon dioxide was passed into this solution, it immediately became colorless, and a crystalline precipitate of **2** separated. The latter was isolated and dried in vacuo while it stayed colorless; yield 1.65 g (96%), mp 152–155°C. IR: 1742, 1728, and 1716 cm^{-1} (CO). Anal. calcd for $C_{22}H_{22}NO_6P$ (427.4): C, 61.82; H, 5.18; N, 3.27; found: C, 61.56; H, 5.50; N, 3.38.

TABLE 2 Crystal Data and Structure Refinement for **6b**

Empirical formula	$C_{32}H_{26}NO_4PS_2$
Formula weight	583.63
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 12.408(4) Å b = 14.396(4) Å c = 16.923(4) Å β = 108.00(2)°
Volume	2874.9(14) $Å^3$
Z	4
Density (calculated)	1.348 Mg/m^8
Absorption coefficient	0.279 mm^{-1}
F (000)	1216
Crystal size	0.53 × 0.43 × 0.40 mm
Θ range for data collection	2.82 to 23.97°
Index ranges	$-14 \leq h\, 0$, $-16 \leq k \leq 0$, $-18 \leq l \leq 19$
Reflections collected	4725
Independent reflections	4495 [R(int) = 0.0101]
Observed reflections ($I > 2\sigma I$)	3518
Absorption correction	Semi-empirical from ψ-scans
Max. and min. transmission	0.9995 and 0.9768
Refinement method	Full-matrix least squares on F^2
Data / restraints / parameters	4495 / 0 / 363
Goodness-of-fit on F^2	1.109
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0381, $wR2$ = 0.0819
R indices (all data)	$R1$ = 0.0567, $wR2$ = 0.0920
Largest diff. peak and hole	0.228 and −0.202 $eÅ^{-3}$

Additional information of the crystal structure determination are deposited at the Cambridge Crystallographic Data Center (CCCD 102537).

When the crystals were dissolved in $CDCl_3$, they immediately lost CO_2 and gave a yellow solution of **1a**.

CS_2-Adducts 4

To a solution of **1a** (3.10 g, 8.32 mmol) in 10 mL of dichloromethane, 2 mL of carbon disulfide, and, after 1 hour, *n*-pentane were added, then yellow crystals of **4a** separated; yield 3.45 g (90%), mp 134–135°C with vigorous decomposition. IR: 1740, 1707 cm^{-1} (CO). ^{31}P NMR: δ(anisole) = −42.9, δ(CDCl$_3$) = 40.0, δ(DMSO) = −25.9. ^{1}H NMR (CDCl$_3$): δ = 2.65 (d, $^2J_{PH}$ = 12.5 Hz, 3H, PCH$_3$), 3.46 (s, 3H, OCH$_3$), 3.80 (s, 3H, OCH$_3$). MS (70 eV, 120°C): *m/z* = 400 (6.4%, M$^+$ − CO$_2$Me), 383 (91.6%, M$^+$ − CS$_2$), 76 (100%, CS$_2^+$). Anal. calcd for $C_{22}H_{22}NO_4PS_2$ (459.5): C, 57.50; H, 4.82; N, 3.04; found: C, 57.25; H, 4.82; N, 2.99.

To a solution of **1b** (3.48 g, 6.87 mmol) in 15 mL of dichloromethane, 2 mL of carbon disulfide was added. After 35 minutes, light yellow crystals of **4b** separated. Yield 3.26 g (82%), mp 146–149°C with decomposition; hardly soluble in usual solvents even on warming. IR: 1742, 1734 cm^{-1} (CO). ^{31}P NMR (CDCl$_3$): δ = 38.3. ^{1}H NMR (CDCl$_3$): δ = 3.38 (s, 3H, OCH$_3$), 3.44 (s, 3H, OCH$_3$). Anal. calcd for $C_{32}H_{26}NO_4PS$ (583.6): C, 65.85; H, 4.49; N, 2.39; found: C, 65.78; H, 4.61; N, 2.44.

Rearrangement of **4b** *to 2-Diphenylthiophosphinylimino-3,4-bis(methoxycarbonyl)-5,5-diphenyl-dihydrothiophene* **(6b)**

A solution of **4b** (2.50 g, 4.28 mmol) in 10 mL of anisole was warmed to 145°C for 1 hour and turned orange red. After 15 hours at room temperature, bright yellow crystals of **6b** (Table 2) had separated; yield 1.85 g (74%), mp 212–213°C. IR: 1755, 1720 (CO), 1650 (CC), 1590 cm^{-1} (CN). ^{31}P NMR (anisole): δ = 53.1. ^{1}H NMR (CDCl$_3$): δ = 3.55 (s, 3H, OCH$_3$), 3.96 (s, 3H, OCH$_3$). MS (70 eV, 120°C): *m/z* = 583 (72.6%, M$^+$), 524 (6.5%, M$^+$ − CO$_2$Me), 308 (80.4%, 524 − Ph$_2$PS, m* = 181.03), 276 (100%, 308 − S^{32}, m* = 247.32), 216 (56.6%, Ph$_2$PS$^+$). Anal. calcd for $C_{32}H_{26}NO_4PS_2$ (583.6): C, 65.85; H, 4.49; N, 2.39; found: C, 65.24; H, 4.42; N, 2.54.

REFERENCES

[1] Schmidpeter, A.; Zeiß W. Angew Chem 1971, 83, 398; Angew Chem Int Ed Engl 1971, 10, 396.

[2] Schmidpeter, A.; von Criegern, T. Angew Chem 1978, 90, 64; Angew Chem Int Ed Engl 1978, 17, 55.

[3] Schmidpeter, A.; von Criegern, T. J Chem Soc Chem Commun 1978, 470.

[4] Schmidpeter, A.; von Criegern, T. Angew Chem 1978, 90, 469; Angew Chem Int Ed Engl 1978, 17, 443.

[5] Schmidpeter, A.; von Criegern, T. Chem Ber 1978, 111, 3747.

[6] Schmidpeter, A.; von Criegern, T. Z Naturforsch B 1978, 33, 1330.

[7] Schmidpeter, A.; von Criegern, T. Chem Ber 1979, 112, 3472.

[8] Schmidpeter, A.; von Criegern, T. Chem Ber 1979, 112, 2762.

[9] Schmidpeter, A.; von Criegern, T.; Groß, J.; Luber, J.; Weinmaier, J. H.; Tautz, H.; Zeiß, W. Chemistry and Application of Organophosphorus Compounds; Naukova Dumka: Kiev, 1981; pp 256–261.

[10] Sheldrick, W. S.; Schomburg, D.; Schmidpeter, A.; von Criegern, T. Chem Ber 1980, 113, 55.

[11] Sheldrick, W. S. Top Curr Chem (Fortschr Chem Forsch) 1978, 75, 1.

[12] Similar rearrangements in which 2-thionoimidazole derivatives isomerize to 2-iminothiazole derivatives are known: (a) Benhaoua, H.; Texier, F.; Toupet, L.; Carrié, R. Tetrahedron 1988, 44, 1117–1126; (b) Morel, G.; Marchand, E.; Foucaud, A.; Toupet, L. J Org Chem 1990, 55, 1721–1727.