The Interlocking of Salicylic Aldehydes and Ketones with a 2*H*-1,2,4,3-Triazaphosphole

Alfred Schmidpeter*, Franz Steinmüller, and Heinrich Nöth[+]

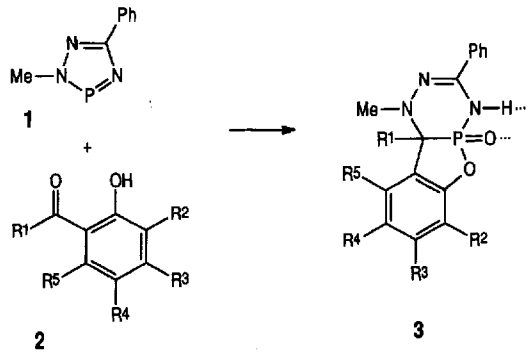
Institut für Anorganische Chemie der Universität München,
Meiserstraße 1, D-80333 München, Germany

Received May 7, 1996

Key Words: Phosphorus heterocycles / *ortho*-Hydroxybenzaldehydes / Phosphonic amide / Michaelis-Arbuzov rearrangement / Hydrogen bonding

Salicylic aldehyde (**2a**) adds to 2-methyl-5-phenyl-2*H*-1,2,4,3-triazaphosphole (**1**) to yield the bicyclic phosphonic amide **3a**. The OH group adds to the P=N bond, the carbon atom of the carbonyl group is inserted into the other P–N bond, and the phosphorus atom is oxidized. In the crystal the compound forms dimers by a double hydrogen bond between two HN–PO units. Substituted salicylic aldehydes as well as *ortho*-hydroxyacetophenone and benzophenone react in the same way.

The phosphorus atom of a 2*H*-1,2,4,3-triazaphosphole such as **1**[1,2] is capable of both accepting and donating a pair of electrons. As a consequence it adds alcohols and other protic nucleophiles to its P=N bond and is oxidized by sulfur or halogen. Alcohols or phenols with appropriate additional functions can at the same time make use of both triazaphosphole reactivities. Glycols, 2-azido alcohols or *o*-heterodienylphenols thus yield spirocyclic phosphoranes[3]. Salicylic aldehyde offers itself as another possible difunctional partner, although the nature of its second function is different. For the reaction with the triazaphosphole phosphorus atom it provides a nucleophilic hydroxyl and an electrophilic carbonyl group at a suitable three-bond distance.



For R[1]-R[5] see Table 1

Results and Discussion

From the benzene solution of 2-methyl-5-phenyl-2*H*-1,2,4,3-triazaphosphole (**1**) and the 2-hydroxybenzaldehydes **2a–d** (R^1 = H, R^2-R^5 = H, OMe, NO_2) or 2-hydroxyacetophenone (**2e**) (R^1 = Me, R^2-R^5 = H) or 2-hydroxybenzophenone (**2f**) (R^1 = Ph, R^2-R^5 = H) products **3a–f** precipitate. They are colorless except for the orange-yellow nitro derivative **3d**. The reaction requires several days at ambient temperature for completion and of course proceeds more rapidly under reflux conditions. The compounds **3** consist of an equimolar combination of the two components as revealed by elemental analysis. It turned out, however, that the product in this case is not a spirocyclic compound[4].

Table 1. ^{31}P- and ^1H-NMR data of **3a–f** in $CDCl_3$; coupling constants in Hz

	3a	**3b**	**3c**	**3d**	**3e**	**3f**
R^1	H	H	H	H	Me	Ph
R^2	H	OMe	H	H	H	H
R^3	H	H	OMe	H	H	H
R^4	H	H	H	NO_2	H	H
R^5	H	H	OMe	H	H	H
$\delta^{31}P$	43.1	41.8	44.9	41.9	45.0	40.9
δ^1H (NCH_3)	3.39	3.29	3.18	3.31	3.15	3.06
$^4J_{PH}$			1.9		1.7	0.7
δ^1H (NH)	8.28	11.49	6.93	8.51	7.97	8.21
δ^1H (R^1)	4.94	5.39	4.73	5.45	1.82	
$^{2,3}J_{PH}$	21.2	20.8	17.8	22.8	16.1	
δ^1H (OCH_3)		3.74	3.68 3.75			

A single-crystal X-ray analysis (see below) revealed the structure of example **3a**. The NMR spectra of all other products (Tables 1 and 2) also correspond to those of **3a**. The phenolic oxygen atom is bound to the phosphorus atom as expected, and the phosphorus atom is oxidized while the carbon atom of the carbonyl group is reduced and inserted into the bond between P-1 and N-2. In this way a dihydro-1,2-benzoxaphosphole and a tetrahydro-1,2,4,5-triazaphosphinine ring are formed and anellated to each other with a phosphonic ester amide group as a bridgehead.

This reaction necessitates a multistep mechanism. The formation of two intermediates, **A** and **B** in the case of **2a**,

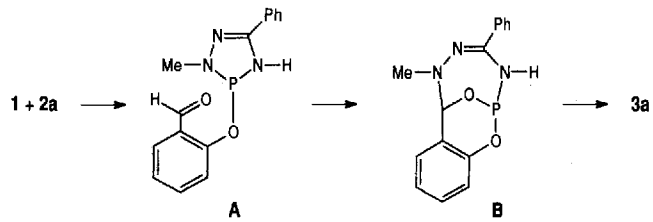
[+]X-ray structure analysis.

  0009–2940/96/1212–1493 $ 15.00+.25/0

although not detected, may be assumed: The first involves the addition of the phenolic group to the P=N bond, a reaction, which can be verified by treatment with phenol. The intramolecular nucleophilic attack of the hydrazino moiety then initiates the addition of the respective PN bond to the carbonyl group[4]. A similar mechanism was claimed for the reaction of aminophosphites with aldehydes[5,6]. The final step consists of an O→P shift of the carbon atom according to a Michaelis-Arbuzov rearrangement. The reaction seems to be restricted to the intramolecular process because the ethanol adduct of **1** does not react with benzaldehyde.

Table 2. ^{13}C-NMR data of **3** in $CDCl_3$; coupling constants J in Hz

	3a	**3b**	**3c**	**3e**	**3f**
δ (NMe)	46.6	46.0	47.6	39.7	41.7
$^3J_{PC}$	19.2	18.9	17.5	14.7	13.6
δ (C-3)	154.6	145.6	59.9	153.1	153.7
$^2J_{PC}$	7.3	8.4	8.5	7.3	6.3
δ (3-Ph,*i*)	132.9	132.6	133.0	132.9	132.9
$^3J_{PC}$	6.6	6.3	6.2	7.3	7.3
δ (3-Ph,*o*)	125.9	125.7	125.8	125.9	125.6
δ (3-Ph,*m*)	128.5	129.4	128.7	128.5	129.0
δ (3-Ph,*p*)	129.8	129.5	129.9	129.8	129.5
δ (C-7)	143.1	142.3	142.9	142.3	140.5
$^2J_{PC}$	6.1	5.2	7.1	4.2	4.2
δ (C-8)	114.1	142.6	91.8	114.3	114.4
$^3J_{PC}$	9.6	8.4	8.9	9.5	9.7
δ (C-9)	130.6	113.3	162.7	130.3	128.5
$^4J_{PC}$	1.1		1.9		
δ (C-10)	123.6	123.5	94.1	123.7	123.7
$^4J_{PC}$	1.7				
δ (C-11)	128.2	119.7	158.8	127.5	128.8
$^3J_{PC}$	17.6	17.6	15.2	15.7	17.8
δ (C-12)	122.3	123.9	102.6	126.4	125.6
$^2J_{PC}$	20.7	20.7	20.4	14.4	17.8
δ (C-13)	57.9	56.6	56.7	58.4	68.3
$^1J_{PC}$	134.9	134.2	136.0	137.4	131.3
δ (R^1,*i*)				16.2	133.3
$^2J_{PC}$				2.1	7.4
δ (R^1,*o*,*m*,*p*)					128.6 128.7 130.8
δ (OMe)		55.8	55.3 55.6		



All NMR data (Tables 1 and 2) are in accord with structure **3**; indicative of the ring enlargement is the ^{31}P coupling to the *N*-methyl protons which decreases from $^3J_{PH}$ = 6.2 Hz in **1**[7] to $^4J_{PH}$ = 0–2 Hz in **3**. Compound **3a** crystallizes from benzene with one molecule of solvent per unit cell which contains two molecules of the compound. The molecular structure is shown in Figure 1, and relevant data are given in Table 3. The dihydrobenzoxaphosphole part is planar (sum of angles in the five-membered ring = 539.8°), the tetrahydrotriazaphosphinine ring has a boat conformation. Dimers are formed by hydrogen bonds between N4–H and P5–O1 of the one and P5–O1 and N4–H of the other molecule (Figure 2). The existence of associates of this type was demonstrated for phosphoric and phosphinic amides in solution by IR and NMR spectroscopy[8–10] and in the crystal by X-ray structure analysis[11]. The dimerization necessitates a *cis* orientation of the NH and PO group which in the case of **3a** is fixed by the ring structure. An alternative way of association of the *cis* or *trans* conformer are single hydrogen bonds between neighbouring amide molecules leading to a polymeric aggregate[11–13]. The distance between the hydrogen-bonded nitrogen and oxygen atom in **3a** (Table 3) is in good agreement with the mean value of known (P)O···H···N distances, 284 pm[14], and in particular with the distances found for phosphoric amide dimers, 286–289 pm[11]; for the hydrogen-bonded polymers

Figure 1. Molecular structure of **3a** (thermal ellipsoids with 25% probability)

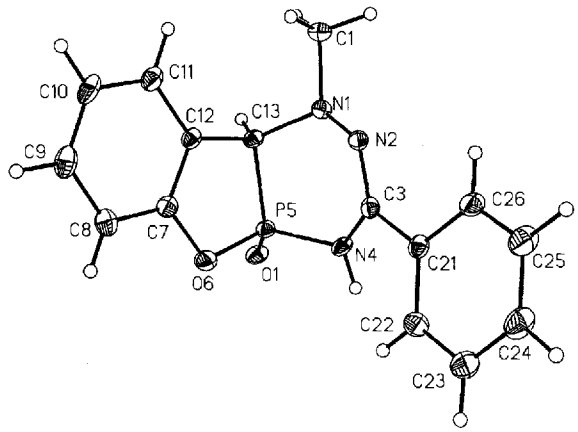
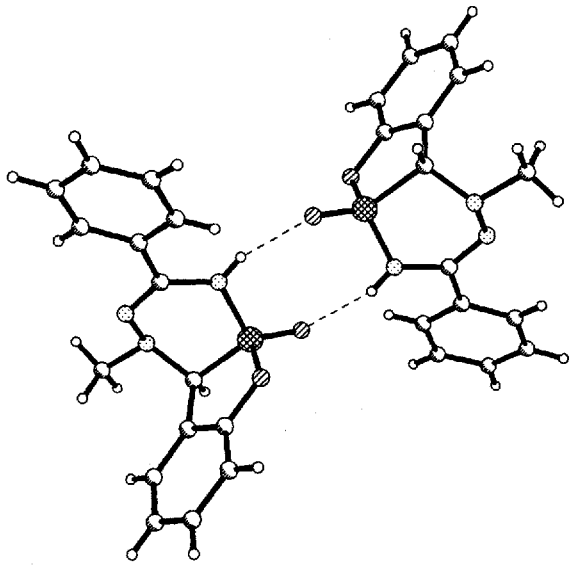


Table 3. Selected bond lengths [pm] and angles [°] of **3a**

N1-C1	146.8(4)	C1-N1-C13	113.2(2)
N1-C13	147.8(4)	C1-N1-N2	108.2(2)
N1-N2	141.0(4)	C13-N1-N2	116.4(2)
N2-C3	128.2(4)	N1-N2-C3	116.5(3)
C3-C21	147.8(4)	N2-C3-C21	118.9(3)
C3-N4	140.8(4)	N2-C3-N4	122.9(3)
N4-P5	164.1(3)	C21-C3-N4	118.2(3)
P5-C13	182.7(3)	C3-N4-P5	120.3(2)
P5-O1	146.4(2)	N4-P5-C13	102.8(1)
P5-O6	162.3(3)	N4-P5-O1	113.8(1)
O6-C7	140.1(4)	N4-P5-O6	107.6(1)
C7-C12	138.7(5)	C13-P5-O1	123.1(1)
C7-C8	138.0(5)	C13-P5-O6	97.0(1)
C8-C9	138.5(5)	O1-P5-O6	110.6(1)
C9-C10	138.7(6)	P5-O6-C7	111.7(2)
C10-C11	138.8(5)	O6-C7-C12	115.6(3)
C11-C12	139.7(4)	C7-C12-C13	112.9(3)
C12-C13	151.5(4)	C12-C13-P5	102.6(2)
N4-O1′	285.6	C12-C13-N1	119.6(2)
N4-H	85.7	P5-C13-N1	108.0(2)
O1′-H	203.3	N4-H-O1′	160.7

Figure 2. Hydrogen-bonded dimer of **3a**



somewhat shorter distances were found, i.e. 276–283 pm[11,13].

Experimental

NMR: Jeol GSX 270 and EX 400, chemical shifts relative to 85% H_3PO_4 and TMS. – Solvents were dried with molecular sieves. – The triazaphosphole **1** was prepared from N^1-methyl benzamidrazone hydrochloride and tris(dimethylamino)phosphane[7].

3a: From the solution of 1.95 g (11.0 mmol) of **1** and 1.17 ml (11.0 mmol) of **2a** in 20 ml of benzene colorless crystals of **3a** · 0.5 C_6H_6 separated after 2 d at room temp. A second crop was obtained from the filtrate after 7 d. The product was dried in vacuo; yield 1.31 g (39%), m.p. 198–200°C. – $C_{15}H_{14}N_3O_2P$ (299.3): calcd. C 60.20, H 4.72, N 14.04; found C 60.84, H 5.28, N 14.34.

3e: A solution of 563 mg (3.14 mmol) of **1** and 331 µl (3.77 mmol) of **2e** in 20 ml of benzene was heated at reflux for 18 h and filtered. After addition of 10 ml of ether, **3d** separated as colorless crystals from the solution at 0°C; yield: 494 mg (46%), m.p. 176–177°C. – $C_{16}H_{16}N_3O_2P$ (313.3): calcd. C 61.34, H 5.15, N 13.41; found C 61.11, H 5.24, N 12.98.

3f: A solution of 313 mg (1.73 mmol) of **1** and 411 mg (2.07 mmol) of **2f** in 15 ml of benzene was heated at reflux for 18 h. The solution was reduced in vacuo to 2 ml, and **3f** separated on standing; yield: 403 mg (55%), m.p. 209–210°C. – $C_{21}H_{18}N_3O_2P$ (375.4): calcd. C 67.20, H 4.83, N 11.19; found 67.01, H 5.05, N 11.05.

Compounds **3b–d** were prepared correspondingly (Table 4).

Crystal-Structure Analysis of **3a** · 0.5 C_6H_6: $C_{18}H_{17}N_3O_2P$ (338.32), crystal size 0.45 × 0.3 × 0.3 mm³, light yellow block, triclinic, space group $P\bar{1}$, a = 8.398(1), b = 10.621(1), c = 10.980(1) Å, α = 118.435(1), β = 92.802(1), γ = 100.486(2)°, V = 836.29(14) Å³, Z = 2, $d_{calcd.}$ = 1.344 Mg m^{-3}, μ = 0.180 mm^{-1}, $F(000)$ = 354. Siemens P4, SMART area detector, Mo-K_α radiation, λ = 0.71073 Å, hemisphere data collection, T = 293(2) K, 2Θ range = 4.28 to 58.00° in $-10 \leq h \leq 10$, $-13 \leq k \leq 11$, $-13 \leq l \leq 13$, collected reflections: 5119, independent reflections: 3271 (R_{int} = 0.0875), observed reflections: 2797 [$F > 4\sigma(F)$]. – Structure solution program: XS (SHELXTL Vers. 5), direct methods, full-matrix least-squares on F^2, hydrogen atoms refined as a riding model, weighting scheme $w^{-1} = \sigma^2F_o^2 + (0.0767\ P)^2 + 1.2179\ P$, $P = (F_o^2 + 2\ F_c^2)/3$, data-to-parameter ratio 15.1:1 (12.9:1 [$F > 4\sigma(F)$]), final R indices [$F > 4\sigma(F)$]: $R1$ = 0.068, $wR2$ = 0.176, GoF on F^2 = 1.176, largest difference peak/hole: 0.386/−0.544 eÅ^{-3}, refinement program: SHELXL (Sheldrick 1993). Further details are available from the Fachinformationszentrum, Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-405214.

Table 4. Preparation of **3b–d**

	3b	**3c**	**3d**
mg (mmol) **1**	530 (2.89)	417 (2.35)	1020 (5.74)
mg (mmol) **2**	700 (4.60)	429 (2.35)	1920 (11.5)
ml benzene/time reflux	20/4 h	20/48 h	40/18 h
mg (%) yield	570 (48)	461 (55)	1410 (47)
m.p. °C	76-77	221-222	195, decomp.

[1] Y. Charbonnel, J. Barrans, *Tetrahedron* **1976**, *32*, 2039–2043.
[2] A. Schmidpeter, J. Luber, H. Tautz, *Angew. Chem.* **1977**, *89*, 554–555; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 546.
[3] A. Schmidpeter, K. Karaghiosoff in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Georg Thieme Verlag, Stuttgart, **1990**, Chapter 6.
[4] In a preliminary account a spirocyclic structure was assumed for the product erroneously[3]. It could have resulted from a nucleophilic attack of the tervalent phosphorus atom in **A** onto the carbon atom of the carbonyl group and a subsequent proton shift from N to O stabilizing the zwitterion.
[5] I. V. Konovalova, A. N. Pudovik, *Russ. Chem. Rev. (Engl. Transl.)* **1972**, *41*, 411–424.
[6] A vinylogue version of this reaction has been found for phosphorus tris(dimethylamide) and 4-benzyl-5-oxazolones: R. K. Bansal, K. Karaghiosoff, A. Schmidpeter, *Chem. Ber.* **1988**, *121*, 2067–2069.
[7] A. Schmidpeter, F. Steinmüller, K. Karaghiosoff, *Heteroatom Chem.* **1994**, *5*, 385–390.
[8] V. I. Shevchenko, A. A. Koval, *Zh. Obshch. Khim.* **1967**, *37*, 1111–1118; *J. Gen. Chem. USSR* **1967**, *37*, 1053–1060.
[9] M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1882–1887.
[10] G. A. Foulds, T. A. Modro, B. P. Rijkmans, *S. Afr. J. Chem.* **1981**, *34*, 72–75.
[11] M. P. du Plessis, T. A. Modro, L. R. Nassimbeni, *J. Org. Chem.* **1982**, *47*, 2313–2318.
[12] A. F. Cameron, F. D. Duncanson, *Acta Cryst. B* **1981**, *37*, 1604–1608.
[13] B. Davidowitz, T. A. Modro, M. L. Niven, *Phosphorus Sulfur* **1985**, *22*, 255–263.
[14] D. E. C. Corbridge, *The Structural Chemistry of Phosphorus*, Elsevier, Amsterdam, **1974**, p. 252.

[96097]