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A hydroxyaminophosphane derived from 2-imidazolidone and its unusual structure in solution

Invited Paper

Olaf Kühl*, Waltraud Heiden

Institute of Biochemistry,
University of Greifswald,
D-17489 Greifswald, Germany

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Abstract: A novel hydroxyamino phosphane was synthesised through the reaction of 2-imidazolidinone with ClPPh2 and subsequently reaction of the resulting bisphosphino derivative with the Grignard reagent $BrMgC_5H_{11}$. The interaction of the pentyl substituent with one of the two phosphino groups and the structure in solution is shown by multinuclear NMR-spectroscopy..

Keywords: *Grignard reaction • Hydroxyaminophosphane • Phosphane • Reduction • „Through-space"-coupling*

1. Introduction

Recently, interest in phosphino urea derivatives as ligands for transition metals has increased [1-5]. The main focus is on the acyclic representatives and therefore the derivatives of urea itself. To avoid difficulties with additional NH-functionalities, the N,N'-dialkyl compounds are usually utilised. In addition, the closely related N-phosphinated carboxylic acid amides were also investigated [1,6,7], although they met with significantly less interest due to their increased sensitivity towards hydrolysis.

In contrast, the cyclic representative of the N,N'-dialkyl ureas, the 2-imidazolidinone, has not been investigated yet. Due to its geometry, its N,N'-bisphosphino derivative can hardly function as a chelate ligand.

Bisphosphino derivates of 2-imidazolidinone seem to be interesting regarding two aspects, the possibility to form bridging polymeric chains or oligomeric rings and the increased reactivity of the carbonyl group due to ring strain. Here, we report on the synthesis of the urea derivative 1,3-bis(diphenylphosphino)-2-imidazolidinone **1** and the product of its reaction with n-pentylmagnesiumbromide.

2. Experimental Procedures

1: To a suspension of 1.0 g (6 mmol) 2-imidazolidinone in 50 mL THF, 1.7 mL (12 mmol) triethylamine and 100 mg 4-(dimethylamino)pyridine are added. A solution of 2.16 mL (12 mmol) $ClPPh_2$ in 10 mL THF is added at ambient temperature. Almost immediately, a voluminous, white precipitate forms and the reaction mixture is stirred for a further 4 h. The precipitate is filtered off and the filtrate reduced *in vacuo*. The white product precipitates upon addition of 30 mL of hexanes.

Yield: 2.72 g (53%) mp.: 121-123°C. ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ = 7.37-7.44 (m, 20 H, Ph), 3.18 (s, 4 H, CH_2); $^{13}C\{^{1}H\}$ NMR (75.5 MHz): δ = 163.6 (t, $^{2}J_{PC}$ = 22.5 Hz, C=O); 135.6 (d, $^{1}J_{PC}$ = 22.5 Hz, i-Ph); 132.5 (d, $^{3}J_{PC}$ = 21.4 Hz, m-Ph); 129.4 (m, o-Ph); 41.4 (d, $^{2}J_{PC}$ = 8.3 Hz, CH_2); $^{31}P\{^{1}H\}$ NMR (121.5 MHz): δ = 34.2 (s); IR (KBr, cm^{-1}): 1702 vst; EI-MS [m/z, %]: 454.3 (M^+, 100), 385.3 ($HN(PPh_2)_2$, 100); 376.4 (M^+ - Ph, 11.7); 348.6 (M^+ - Ph-CO, 10.5); 300.7 (M^+ - 2 Ph, 1); 268.3 (M^+ - PPh_2, 31.48); 261.4 (PPh_3, 5.0); 183.4 (PPh_2, 35.0); C,H,N-analysis: calc. (%) for $C_{27}H_{24}N_2OP_2$ (454.38): C 71.37; H 5.32; N 6.17; found: C 70.33; H 5.75; N 5.68.

* *E-mail: dockuhl@gmail.com*

2: 493 mg (1.08 mmol) of **1** are disolved in 20 mL THF at ambient temperature and 1.68 mL of a 0.65 M solution of pentylmagnesiumbromide in THF added dropwise and the reaction mixture stirred for 2 h. Subsequently, NH_4Cl and then 0.2 mL degassed water are added and the reaction mixture stirred overnight. The solution is filtered and reduced *in vacuo* to dryness. The residue was dissolved in 10 mL toluene, reduced to dryness *in vacuo*, dissolved in 10 mL CH_2Cl_2, filtered, the filtrate reduced *in vacuo* and the product precipitated with hexanes.

Yield: 530 mg (93%). mp.: 94-96°C (softening), 111-113°C (viscous oil).

^{1}H NMR (300.1 MHz; $CDCl_3$; 25°C): δ = 7.81-7.20 (m, 20 H, ArH); 6.05 (s, 1 H, OH); 3.40 (t, ^3J = 8.4 Hz; 2 H; NC^4H_2); 3.25 (t, ^3J = 8.2 Hz; 2 H; NC^5H_2); 2.03 (t, ^3J = 7.8 Hz; 2 H; CH_2); 1.43-1.28 (m, 6 H, CH_2); 0.85 (t, ^3J = 7.2 Hz; 3 H; CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz): δ = 139.0 (d, J_{PC} = 13.1 Hz; C_2); 135.5 (m, i-C); 132.5 (m, m-C); 129.4 (s, p-C); 128.4 (m, o-C); 42.31 (d, J_{PC} = 10.57 Hz, C_4); 39.05 (s, C_5); 33.04 (d, J_{PC} = 12.83 Hz; C_b); 27.68 (d, J_{PC} = 11.32 Hz; C_a); 25.31 (d, J_{PC} = 15.1 Hz; C_c); 21.97 (s, C_d); 13.65 (s, C_e); minor set of alkyl signals (*syn* form) at 38.40 (s, $C_{4'}$ and $C_{5'}$); 30.05 (s,$C_{b'}$); 28.60 (s, $C_{a'}$); 23.44 (s, $C_{c'}$); 21.76 (s, $C_{d'}$); 10.68 (s, $C_{e'}$); ^{31}P NMR (121.5 MHz): δ = 31.17 (s, P^3); -15.75 (quintet, $^{5,6}J_{PH}$ = 7.2 Hz; P^1); C,H,N-analysis calc. for $C_{32}H_{36}N_2OP_2$ (526.53): C 72.99 H 6.89 N 5.32; found: C 72.13 H 7.02 N 4.98.

3. Results and Discussion

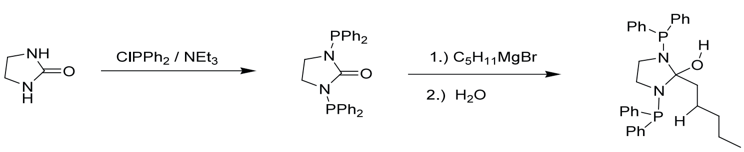
2-Imidazolidinone reacts with two equivalents of $ClPPh_2$ in the presence of triethylamine as auxiliary base and a catalytic amount of 4-(dimethylamino)pyridine to give **1**. Compound **1** is then reduced in a standard Grignard reaction with $BrMgC_5H_{11}$ in THF and subsequent hydrolysis with degassed water to the corresponding hydroxyaminophosphane **2** (Eq. 1).

The reaction of an acyclic bisphosphino urea like $(PPh_2NMe)_2CO$ with $BrMgC_5H_{11}$ or BuLi was unsuccessful. In any such attempts, the starting material was recovered near quantitatively. The attempted reduction with $LiAlH_4$ resulted in the cleavage of the P-N bond [8]. Therefore, the reaction is so far limited to derivatives of the cyclic urea compound **1**.

The urea derivative **1** is a symmetric compound with medium solubility in most organic solvents except alkanes, where it is insoluble. The ^{31}P-$\{^1H\}$-NMR spectrum shows a single signal at δ = 34.2 and thus in the same region as the known compound $(Ph_2PNH)_2CO$, but significantly shifted upfield compared to the dimethyl urea derivatives [4]. The signal for the carbonyl carbon atom in the $^{13}C\{^1H\}$-NMR (δ = 163.6, t, $^2J_{PC}$ = 22.5 Hz) and the IR-spectrum (1702 cm^{-1}, st) are as expected. Neither in the IR nor in the ^{1}H-NMR spectrum could we find a signal indicative of a NH-group, as would be expected in an only partial reaction.

Reaction of **1** with n-pentylmagnesiumbromide yields **2** almost quantitatively. The IR-spectrum shows a typical OH-band at 3615 cm^{-1}, but neither a NH- nor a CO-band. Surprisingly, the $^{31}P\{^1H\}$-NMR spectrum of **2** reveals two signals at 31.2 and –15.7 ppm, respectively. Whereas the signal at 31.2 ppm is almost unchanged compared to the respective signal in **1**, the other signal is shifted upfield by Δδ = –46.9 ppm. Such a strong upfield shift cannot be explained by axial and equatorial positions in a five-membered ring, since those explain only differences in the region of 2-5 ppm [9]. The $^{13}C\{^1H\}$-NMR spectrum of **2** shows likewise several unexpected signals in the region typical for alkyl groups. It includes a series of five signals between 35 and 10 ppm that can be attributed to the n-pentyl substituent. However, most of these signals are doublets with a relatively large PC coupling constant (Scheme 1). Indexation of the signal was achieved with a C,H-COSY spectrum. Coupling over so many bonds is extremely unusual for saturated carbon chains, especially since only one of the two ring carbon atoms shows PC coupling.

To solve this contradiction, a ^{31}P-NMR experiment was conducted. It could be shown that the upfield signal exhibits a quintet due to PH coupling with a coupling constant of 7.2 Hz. The CH_2 protons in the ring show no coupling to phosphorus in the ^{1}H-NMR spectrum. The upfield shifted phosphorus atom is seemingly engaged in magnetic „through space“ interactions with two CH_2 groups of the pentyl substituent that result in PC- and PH-couplings responsible for the upfield shifts in the ^{31}P-NMR spectrum. The two CH_2 groups are those labelled C_b and C_c. It is also evident that the phosphorus signal at δ = 31.2 ppm shows the signal for one of the phosphorus atoms in the *anti*-conformation



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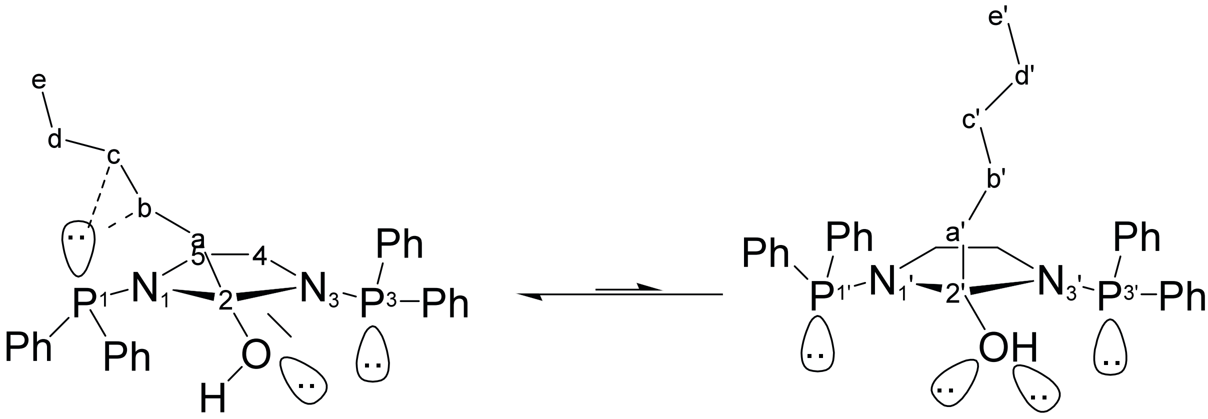

Anti

Syn

C_2: 139.0 (d, 13.0 Hz)
C_4: 42.31 (d, 10.57 Hz)
C_5: 39.05 (s)
C_a: 27.68 (d, 11.32 Hz)
C_b: 33.04 (d, 12.83 Hz)
C_c: 25.31 (d, 15.1 Hz)
C_d: 21.97 (s)
C_e: 13.65 (s)

$C_{2'}$: not observed
$C_{(4,5)'}$: 38.40 (s)

$C_{a'}$: 28.60 (s)
$C_{b'}$: 30.05 (s)
$C_{c'}$: 23.44 (s)
$C_{d'}$: 21.76 (s)
$C_{e'}$: 10.68 (s)

Scheme 1. $^{13}C\{^1H\}$ NMR data for 2 and structure in solution

superimposed on the signal for the tqo equivalent phosphorus atoms of the *syn*-conformation.

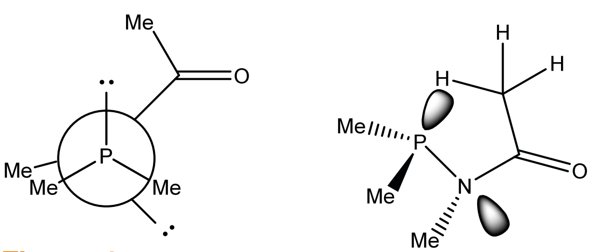

Figure 1. Conformation dependence of the coupling in N-methyl, N-dimethylphosphinoacetamide.

The structure determination of **2** with the NMR-data was solved by comparison of the spectra of N-methyl, N-dimethylphosphinoacetamide (Fig. 1) [10] and the urea derivatives $Ph_2PN(R)C(O)NHR'$ (R, R' = Ph, Et) [11]. Similar observations were made in phosphinonaphthophenols [12]. Each of the two phosphino substituents can orientate its lone pair towards the lone pairs of the OH-groups or have it pointing away from them. This results in an *anti*- and two *syn*-conformations of the phosphino groups. Within the *anti*-conformation, the lone pair on phosphorus points towards the OH-group and causes a strong coupling with the carbon atoms C_2 and C_4. The other phosphorus atom causes no or only very weak couplings to the carbon atoms C_2 and C_5, since its lone pair points away from the OH-group [13]. Following these arguments, a singlet or a triplet is expected for C_2 in the ^{13}C-$\{^1H\}$-NMR spectrum for the two *syn*-conformations and either two singlets or two doublets for C_4 and C_5. In the *syn*-conformation shown in Scheme 1, we would expect a triplet for $C_{2'}$ and a doublet for $C_{4'}$ and $C_{5'}$, respectively. In reality, we observe the spectrum for the *anti*-conformation. Within the *anti*-conformation, the phenyl rings of one phosphorus atom are on the same side of the central imidazolidone ring as the pentyl substituent. This restricts the rotation of the pentyl substituent and the carbon atoms C_b and C_c come in close proximity to the lone pair of the other phosphorus atom. This results in the observed upfield shift of the respective phosphorus atom in the ^{31}P-NMR spectrum and accompanying PH-coupling as well as PC-coupling in the ^{13}C-$\{^1H\}$-NMR spectrum. The observation of a quintet in the ^{31}P-NMR spectrum is either due to a simultaneous interaction with both CH_2-groups or, more likely, a dynamic interaction with both groups that is not resolved on the NMR time scale. Unfortunately, it was not possible to distinguish between the two possibilities using low temperature NMR. A second, weak group of signals in the alkyl range of the ^{13}C-{^1H}-NMR spectrum is due to the presence of one of the *syn*-conformations that could possibly be in equilibrium with the *anti*-conformation. The assignment of the *syn*-conformation (Scheme 1) was performed using the coupling pattern in the pentyl substituent.

Ring opening due to fissure of a N-C(O) bond would result in a acyclic N-phosphino carboxylic acid amide of the formula $PPh_2N(H)(CH_2)_2N(PPh_2)C(O)C_5H_{11}$. Such a compound would be very sensitive to hydrolysis resulting in the loss of the phosphino group at the amide nitrogen. The compound will have to feature a NH- and a CO-band in the IR-spectrum that were not observed. Furthermore, we would expect a broad doublet in the ^{31}P-NMR spectrum due to coupling with the NH proton, but not further coupling to the CH_2-groups. Additionally, we might observe a triplet splitting of a doublet, but not the quintet we actually observe. Such a compound would not feature PC couplings to two CH_2-groups of the pentyl substituent in the ^{13}C-{^1H}-NMR spectrum, as observed, but with one CH_2-group of the ethyl bridge of the opened imidazole. Therefore, an acyclic compound can safely be excluded after perusal of the spectroscopic data.

Conclusion

The reaction of a cyclic or acyclic N,N'-dialkyl urea derivative results in the formation of the N,N'-bisphosphino urea compound, but only the cyclic derivative could be reduced to the corresponding alcohol using a Grignard reagent. Attempts to do so with the acyclic urea compound resulted in hydrolysis and loss of the phosphino groups.

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