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The reactivity of acyl chlorides towards sodium phosphoethynolate, Na(OCP): a mechanistic case study†

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The reaction of Na(OCP) with mesitoyl chloride delivers an ester functionalized 1,2,4-oxadiphosphole in a clean and P-atom economic way. The reaction mechanism has been elucidated by means of detailed NMR-spectroscopic, kinetic and computational studies. The initially formed acyl phosphaketene undergoes a pseudo-coarctate cyclization with an (OCP)[−] anion under the loss of carbon monoxide to yield a five-membered ring anion. Subsequently, the nucleophilic attack of the formed heterocyclic anion on a second acyl chloride molecule results in the 1,2,4-oxadiphosphole. The transient acyl phosphaketene is conserved during the reaction in the form of four-membered ring adducts, which act as a reservoir. Consequently, the phosphoethynolate anion has three different functions in these reactions: it acts as a nucleophile, as an en-component in [2 + 2] cycloadditions and as a formal P[−] transfer reagent.

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Introduction

Decarbonylation reactions, such as the transformation of aldehydes¹ into hydrocarbons, are widely utilized for the removal of carbonyl groups in organic syntheses.² As special congeners of carbonyl compounds, ketenes can undergo photochemical decarbonylation, yielding carbenes as reactive species.³ Analogously, decarbonylation reactions of phosphaketenes R–P=C=O have been described.⁴ These photochemical⁵ or transition metal assisted⁶ reactions deliver – *via* the cleavage of the PC double bond – transient phosphinidenes or phosphinidene complexes, respectively. Recently, we reported the synthesis of several hetero-phosphaketenes employing the phosphoethynolate (OCP)[−] anion as a phosphorous nucleophile. Furthermore, the ambident character of this anion has been demonstrated.⁷ According to the analysis of the natural resonance structures, the weighting of the phosphoethynolate mesomeric structure **1b** is slightly larger than that of **1a** (Fig. 1).^{7b} Besides these two predominant structures, though with a much smaller weighting, structure **1c** contributes to the electronic ground state. It describes the (OCP)[−] anion as

a donor–acceptor complex of a P[−] ion and carbon monoxide. Similar to the description of a transition metal carbonyl complex, the CO unit acts as a σ-donor and a π-acceptor.

The delocalization of the negative charge hampers the spontaneous decarbonylation of the (OCP)[−] ion, however, the contribution of the mesomeric structure **1c** suggests that this anion may act as a (formal) P[−] transfer reagent. Indeed, we could demonstrate that the reaction of an imidazolium salt with Na(OCP) forms the adduct of the parent phosphinidene (P–H) with the corresponding N-heterocyclic carbene.⁸ According to the proposed mechanism, the parent phosphaketene (H–P=C=O) is formed as an intermediate, which delivers the PH fragment in a concerted reaction step under the extrusion of CO.⁹ The (OCP)[−] anion was found to be a useful synthon to obtain heterocycles and cages,¹⁰ especially when accompanied by the cleavage of the C–P bond.¹¹ In general, in this way, anionic phosphorous heterocycles are accessible and there are two possibilities: (i) the CO moiety can still be incorporated in the final product as a carbonyl group or (ii) carbon monoxide may be released in the reaction as a gaseous by-product. When Na(OCP) is reacted with two equivalents of a small carbodiimide¹² or an activated alkyne (PhC≡C–CO₂Et),^{11a} substituted

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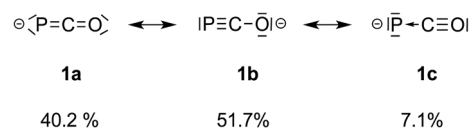


Fig. 1 Resonance structures of the phosphoethynolate anion.



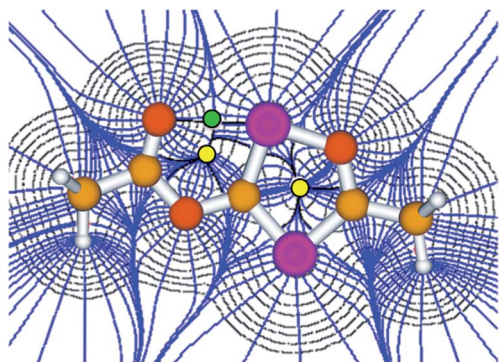


Fig. 3 Atoms in molecules (AIM) analysis of **3'** at the B3LYP/6-311+G** level of theory. The green and yellow dots represent the bond and ring critical points, respectively.

³¹P-NMR spectroscopy. At $-35\text{ }^{\circ}\text{C}$ the parallel formation of two intermediates **A** and **B** was observed. NMR investigations at different temperatures indicated that **B** is in equilibrium with **A** and an $(\text{OCP})^-$ anion. Intermediates **A** and **B**, the final product **3** and $\text{Na}(\text{OCP})$ are the only species which can be detected using ³¹P-NMR spectroscopy. NMR experiments using different stoichiometric ratios of the starting materials did give the same results.

Anion **A** and dianion **B** were identified using GIAO chemical shift calculations, which are shown in Fig. 4 together with the

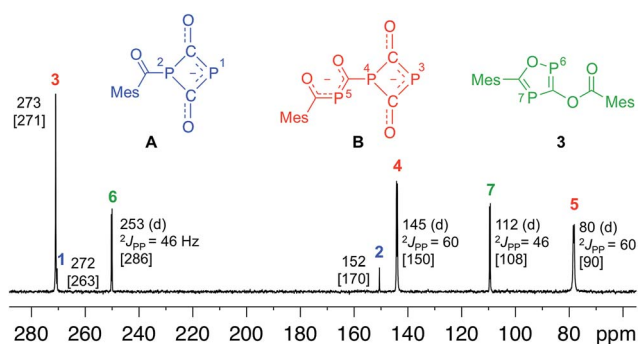


Fig. 4 ³¹P-NMR spectrum at $-35\text{ }^{\circ}\text{C}$ after 17 h reaction time showing intermediates **A**, **B** and the final product **3**. Chemical shifts are given in ppm, coupling constants (J) in Hz. Calculated chemical shifts at the B3LYP/aug-cc-pVDZ level are given in brackets.

experimental data. **A** and **B** are adducts of a mesityl phosphaketene molecule with one and two $(\text{OCP})^-$ ions, respectively. This indirectly indicates the initial formation of mesityl phosphaketene, $\text{MesCO-P}=\text{C}=\text{O}$. The common structural motif of **A** and **B** is the four-membered $\text{P}(\text{CO})_2\text{P}$ ring, which was first described for $[\text{O}_2\text{C-P}(\text{CO})_2\text{P}]^{2-}$, the adduct of a CO_2 molecule and two $(\text{OCP})^-$ ions.^{14c} The ³¹P-NMR chemical shifts of this adduct ($\delta = 279$ and 102 ppm) are indeed very similar to those of the rings in **A** and **B**. The ³¹P-NMR chemical shift of the P5 (80 ppm) atom in **B** matches well with that of bismesityl phosphide $[\text{P}(\text{COMes})_2]^-$, ($\delta = 86$ ppm).²⁶

At this point, it is not obvious how the intermediates **A** and **B** are involved in the formation of **3**. We therefore reacted 2,4,6-trimethylbenzothioyl chloride (**4**) with $\text{Na}(\text{OCP})$ in the hope of identifying another possible intermediate. When $\text{Na}(\text{OCP})$ and **4** were reacted at $-78\text{ }^{\circ}\text{C}$ in a ratio of 2 : 1, again gas evolution indicated the formation of carbon monoxide. Using NMR spectroscopy we could observe the formation of the anion **5**, which was isolated in low yield (Scheme 2). The structure of **5** with a sodium counter ion was unambiguously determined using single crystal X-ray diffraction analysis (see Fig. 5).

Compound **6**, which is the disulfur analogue of **3**, was not formed even when thioacyl chloride was used in excess. However, when **5** was reacted with mesityl chloride, the 1,2,4-thiadiphosphole **7** was obtained as the monosulfur analogue of **3**.²⁷ The outcome of these experiments is in line with the lower electrophilicity of thioacyl chlorides when compared to acyl chlorides. Importantly, these results also give further hints to a possible reaction mechanism for the formation of oxadiphosphole **3**. We assume that in the last step a mesityl chloride

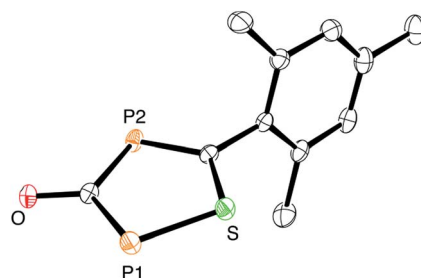
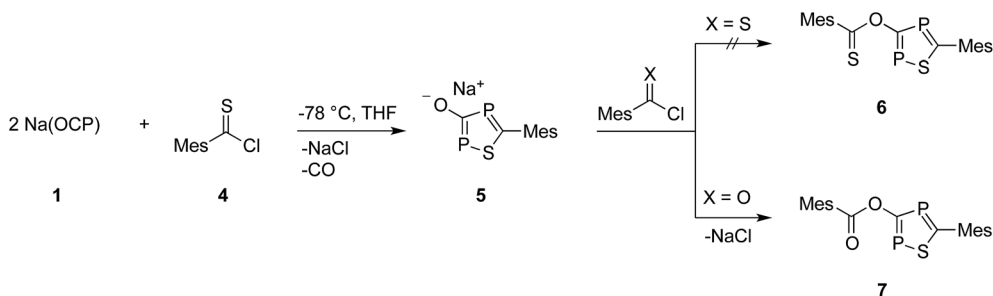
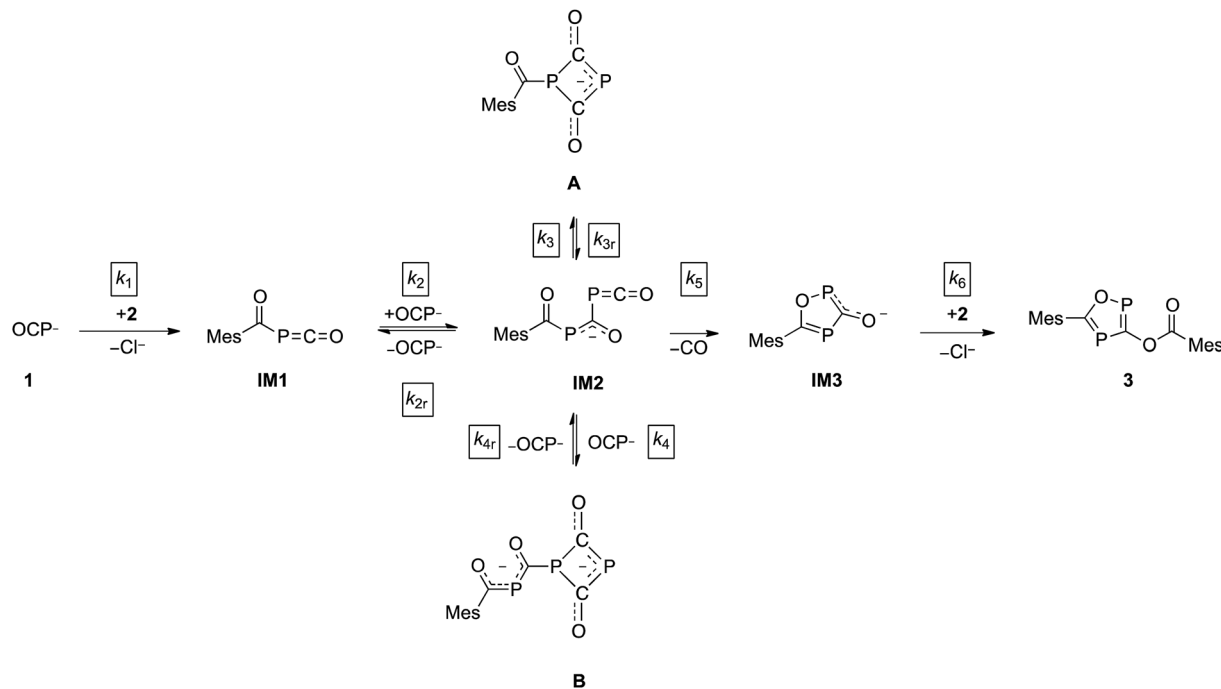


Fig. 5 ORTEP plot of **5** (thermal ellipsoids are drawn at 50% probability). The sodium counter ion with two coordinated DME molecules and hydrogen atoms have been omitted for clarity.



Scheme 2 Formation of sodium 1,2,4-thiadiphosphol-3-olate (**5**) and its reaction with (thio)acyl chloride.



Scheme 3 Proposed reaction mechanism leading to **3**.

molecule reacts with a 1,2,4-oxadiphosphol-3-olate anion, which is the oxygen analogue of **5**. However, this anion was not observed in the ^{31}P -NMR spectra, which implies that it rapidly reacts further with acyl chloride.

The direct observation of intermediates **A** and **B**, as well as the indirect evidence for the 1,2,4-oxadiphosphol-3-olate anion, allowed us to propose a reaction sequence for the formation of **3** which is shown in Scheme 3.

In the first step, the acyl phosphaketene forms as intermediate **IM1**. This is subsequently attacked by an $(\text{OCP})^-$ ion, leading to **IM2**. From intermediate **IM2**, which was not observed experimentally, the cyclic anions **A**, **B** and **IM3** can be formed. A [2 + 2] ring closure of **IM2** leads to its isomer **A**, while a formal cycloaddition of **IM2** with another equivalent of $(\text{OCP})^-$ anion delivers intermediate **B**. Presumably, the reactions leading from **IM1** to **IM2** as well as from **IM2** to the intermediates **A** and **B** are reversible. This is supported by the experimentally observed equilibrium between **A**, an $(\text{OCP})^-$ anion and **B** (*vide supra*).²⁸ Furthermore, **IM2** can undergo a cyclization under the loss of CO to yield **IM3**. In the final step, the nucleophilic substitution on an acyl chloride with **IM3** gives the final product **3**.

Under the assumption that the reaction mechanism shown in Scheme 3 is correct, a kinetic study was carried out in THF as solvent. The reaction progress was followed at $-35\text{ }^\circ\text{C}$ using ^{31}P -NMR spectroscopy and the concentrations of $\text{Na}(\text{OCP})$, **A**, **B** and the final product **3** were determined from the relative integrals of the corresponding peak areas (see Fig. 6). Applying non-linear fitting to these data, the rate constants for the reaction steps shown in Scheme 3 were estimated (see Table 1). As certain species could not be included in the fitting (either they are not observable on the NMR time scale or do not contain P atoms), this method cannot exclude the possibility of other (slightly

different) reaction pathways. However, the fitted model describes the concentration time dependency of the reaction system reasonably well and gives rate constants within a sensible range.

In this model, the nucleophilic substitution of Cl^- in mesityl chloride for $(\text{OCP})^-$ is slower than the subsequent reaction of the activated acyl phosphaketene MesCO-P=C=O **IM1** with another equivalent of $(\text{OCP})^-$. Indeed, this reaction between **IM1** and $(\text{OCP})^-$ is the fastest of all and explains why **IM1** is not observed. Intermediate **IM2** – likewise not observed – is consumed by four competing reactions: the back reaction to **IM1** and $(\text{OCP})^-$, the reversible formation of **A**, the reversible formation of **B**, which is faster than that of **A** (*i.e.* $k_4 > k_3$), and the irreversible formation of **IM3** which is faster than that of **A** (*i.e.* $k_5 > k_3$) but smaller than that of **B** (*i.e.* $k_5 < k_4$). That **A** and **B**

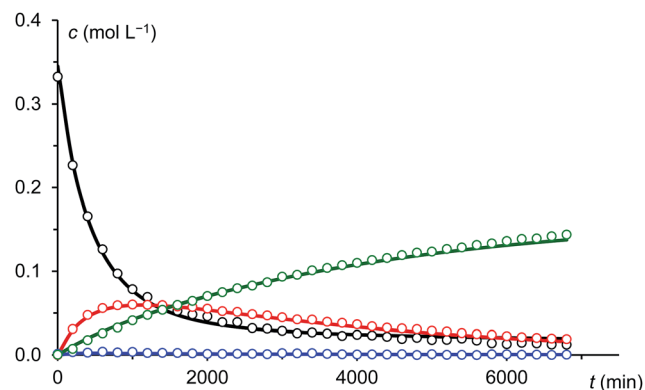
Fig. 6 Measured (dots) and fitted (solid lines) concentrations of $\text{Na}(\text{OCP})$ (black), **A** (blue), **B** (red) and **3** (green).

Table 1 Estimated rate constants (for first order reactions in min^{-1} , for second order in $\text{L} \times \text{mol}^{-1} \times \text{min}^{-1}$), see Fig. 6. The last step of the reaction is instantaneous, thus k_6 is assumed to be much faster than the others and is not listed

Forward reaction		Reverse reaction	
k_1	2.36×10^{-3}	k_{2r}	1.47
k_2	4.98	k_{3r}	5.02×10^{-3}
k_3	2.08×10^{-2}	k_{4r}	3.64×10^{-4}
k_4	8.40×10^{-1}		
k_5	8.19×10^{-2}		

are transient but observable species is due to the slow back reaction to **IM2**, especially for **B** \rightarrow **IM2** which has the smallest rate constant, k_{4r} . Consequently, the concentration of **B** increases steeply at the beginning of the reaction (in the first ca. 15 hours) and serves as a reservoir for intermediate **IM2**. Similarly, **A** is a conserved form of **IM2**, however in this case the accumulation effect is much less pronounced (k_3 is similar to k_{3r}) and the concentration of **A** is low and remains approximately constant throughout the reaction. **IM2** is consumed irreversibly under loss of CO to give **IM3**, which rapidly and irreversibly reacts with acyl chloride to give the final product **3**.

In the present work, the reactions leading from **IM2** to **A** and **IM2** to **B** were not investigated computationally, since similar transformations were subjects of a previous study.²⁸ The formation of **IM3** from **IM2**, however, deserves a closer look. High-level calculations revealed that this reaction follows a concerted mechanism and the activation barrier was found to be low ($4.0 \text{ kcal mol}^{-1}$ at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G* level of theory). The structure of the corresponding transition state is shown in Fig. 7 and the geometrical parameters indicate a late transition state. The cleavage of the P=C double bond of the phosphaketene moiety occurs simultaneously with the formation of the P–O bond. A continuous change in the atom distances was observed along the reaction coordinate. In this process, the starting material, which consists

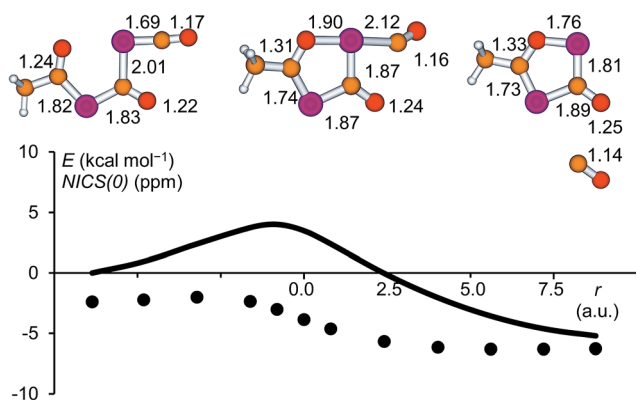


Fig. 7 Relative energy (solid line, CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G*) and NICS(0) values (dots, B3LYP/6-311+G**//B3LYP/6-31+G*) along the reaction coordinate for the ring closure reaction leading from **IM2** to **IM3**. Selected atom distances are given in Å for **IM2**, the transition state and **IM3**.

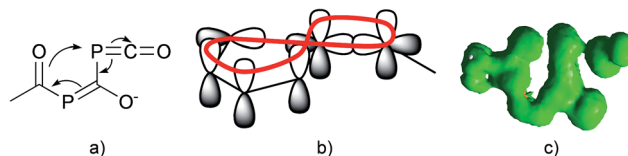


Fig. 8 (a) Coarctation at the P atom of the phosphaketene unit; (b) Möbius type eight-electron interaction; (c) ACID plot of the transition state (isosurface value: 0.020 a.u.) at the CGST/B3LYP/6-31+G* level.

of a phosphaketene unit and a separate delocalized OCPCO moiety, transforms to a moderately aromatic system. The increase in aromaticity is reflected by the NICS(0) values depicted as a function of the reaction coordinate, which become continuously more negative.

Since there is an exocyclic part involved in this bond transformation process, we propose that this reaction is of coarctate type. Besides classical linear and pericyclic reactions, a third group of reactions was classified by Herges as coarctate.²⁹ Coarctate (or complex) reactions proceed in a concerted manner by breaking and making two bonds at one (or more) atoms at a time. In a pericyclic reaction the bond making and bond breaking occurs simultaneously in a cyclic pathway. On the contrary, the coarctate transition state exhibits a so-called coarctate atom (see Fig. 8a), at which the loop of overlapping orbitals is compressed (coarctated). Analogous to pericyclic reactions, the transition state of coarctate reactions is stabilized by orbital interactions, which can be either Hückel or Möbius type. The transition state leading to **IM3** is stabilized by a Möbius type eight-electron interaction and the coarctation of the orbital loop is at the P atom (see Fig. 8b). Coarctate reactions can be further classified as real or pseudo-coarctate reactions. In the latter, the electron delocalization includes a disconnection. Pseudo-coarctate reactions typically exhibit planar transition states and low activation barriers. Since the transition state TS(**IM2** \rightarrow **IM3**) is almost planar and the barrier is very small, we propose that this reaction has pseudo-coarctate character. This is further supported by the ACID (anisotropy of induced current density) plot³⁰ (Fig. 8c), which shows a disconnection in the topology of the delocalized electrons.³¹ Similarly, the fragmentation of 3-azidoacrylaldehyde to isoxazol and dinitrogen has been described and classified as a pseudo-coarctate process.³²

Conclusion

In conclusion, we have presented a one-pot synthesis for substituted 1,2,4-oxadiphospholes, utilizing Na(OCP) as the phosphorous source. The reaction is remarkably selective and atom economic with respect to phosphorous and excellent yields can be obtained. The (OCP)⁻ anion was found to react as a nucleophile and P⁻ transfer reagent. The stepwise reaction mechanism was deciphered using low temperature ³¹P-NMR spectroscopy, kinetic measurements and theoretical calculations. Several [2 + 2] cycloaddition products were observed as intermediates using ³¹P NMR spectroscopy and identified with the help of chemical shift calculations, which demonstrate the performance



of these theoretical methods. The formation of another, not yet observed, intermediate was made plausible through the reaction of Na(OCP) with a thioacyl chloride which gave a stable sodium 1,2,4-thiadiphosphol-3-olate. As observed previously in reactions with isocyanates¹³ and carbon dioxide,^{11c} a remarkable feature in the reactions between (OCP)⁻ salts and heterocumulenes is the equilibrium, X=Y=Z + (OCP)⁻ ⇌ [XY(PCO)Z]⁻, which indicates the stability of the (OCP)⁻ anion with respect to its addition products. The final formation of the oxadiphosphole ring proceeds in a concerted, pseudo-coarctate reaction step. This transformation is reminiscent of reactions seen with α,β-unsaturated organic azides and indicates a possible resemblance between the isovalence electronic (OCP)⁻ and (N₃)⁻ anions.

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