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

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The reaction of Na(OCP) with mesityl 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 phosphaethynolate 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.

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 phosphinidines or phosphinidene complexes, respectively. Recently, we reported the synthesis of several hetero-phosphaketenes employing the phosphaethynolate (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 phosphaethynolate 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),13a substituted

Fig. 1 Resonance structures of the phosphaethynolate anion.

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six-membered phosphorous heterocyclic anions bearing the P atom and the carbonyl functionality in the 1,4-position are formed. However, with the more reactive diethyl acetylenedicarboxylate, besides the analogous six-membered ring, a substituted phospholide $[\text{PC}_4(\text{COOEt})_4]$ was also obtained, accompanied by the loss of carbon monoxide. In a similar reaction, $(\text{OCP})^{-}$ and two equivalents of isocyanate formed five-membered azadiphospholides, which were found to be active catalysts for isocyanate trimerization via spiro phosphoranes. Furthermore, the phosphorous analogues of isocyanates, phosphaketenes, were also reacted with Na(OCP), resulting in triphosphides in a cycloaddition–decarbonylation process in which short-lived intermediates were identified using low-temperature NMR spectroscopy for the first time. In order to understand the reaction pathways leading to these heterocycles, significant computational efforts have been made, but the decarbonylation process still lacks a fundamental understanding.

Here, we report the results of our investigations on the reactivity of Na(OCP) towards acyl chlorides. We provide the mechanistic understanding of a rather complex but selective reaction, which employs the $(\text{OCP})^{-}$ anion as both P nucleophile and P$^+$ transfer reagent.

### Results and discussion

Initially, we attempted to synthesize acyl phosphaketenes RC(O)(P$=$C$=$O), which are the heavier analogues of acyl isocyanates. Knowing that sterically demanding groups are needed to stabilize a phosphaketene in a monomeric form, in the first experiment Na(OCP)(dioxane) was reacted with the rather bulky 2,4,6-trimethylbenzoyl chloride, MesCOCl, in a 1 : 1 ratio (Scheme 1). The precipitation of sodium chloride and a little gas evolution was observed during the reaction. Subsequent investigation of the reaction solution using $^{31}$P-NMR spectroscopy showed no resonance in the expected aromatic delocalization. This is in agreement with previous theoretical studies, which stated that the aromaticity of the parent 1,2,4-oxadiphosphole is just slightly smaller than that of furan and other phosphasubstituted furans. Nuclear independent chemical shift calculations revealed that the ester substituent has only a very small influence on the aromaticity of the five-membered ring. A striking feature of the structure shown in Fig. 2 is the rather short P1–O3 distance (2.5 Å), which is significantly smaller than the sum of the van der Waals radii of phosphorous and oxygen (3.32 Å), indicating a secondary interaction. Note that the oxygen atom O3 of the carbonyl group faces the phosphorous atom P1, which is positively polarized by the neighboring O1 atom. A topological analysis of the electron density on a model system $\text{O}^3$ (methyl instead of mesityl groups) shows a bond critical point between P1 and O3 (see Fig. 3). The corresponding electron density of $\rho = 0.029$ a.u. indicates a relatively strong interaction in the range of hydrogen bonds.

Since four equivalents of reactants are involved [2 MesCOCl + 2 Na(OCP)], a rather complex reaction mechanism with a number of steps must be involved in the formation of 3. To explore the reaction sequence, low temperature NMR measurements were performed. At room temperature the reaction is complete within mixing time of the reagents. A THF solution containing stoichiometric amounts of the starting materials was gradually warmed from −50 °C to room temperature and the progress of the reaction monitored using complicated techniques are needed to separate the desired product from large amounts of by-product. The reaction of the easily accessible Na(OCP) with MesCOCl offers a straightforward synthesis with a good atom economy with respect to phosphorous.

The structure of 3 is shown in Fig. 2. The oxadiphosphole ring and the attached ester moiety are coplanar, while the mesityl rings are rotated out of this plane by 44.2 and 84.5°. The PC and CO bond lengths of the P$\equiv$O ring are comparable to those in other 1,3-oxaphospholes.

Although the P–C bond lengths indicate a Lewis valence electron distribution with alternating single (C1–P2) and double bonds (C1–P1 and C2–P2), some extent of bond length equalization can be observed, which indicates a moderate aromatic delocalization. This is in agreement with previous theoretical studies, which stated that the aromaticity of the parent 1,2,4-oxadiphosphole is just slightly smaller than that of furan and other phosphasubstituted furans. Since the P–C bond lengths indicate a Lewis valence electron distribution with alternating single (C1–P2) and double bonds (C1–P1 and C2–P2), some extent of bond length equalization can be observed, which indicates a moderate aromatic delocalization. This is in agreement with previous theoretical studies, which stated that the aromaticity of the parent 1,2,4-oxadiphosphole is just slightly smaller than that of furan and other phosphasubstituted furans.
31P-NMR spectroscopy. At −35 °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 (OCP)− anion. Intermediates A and B, the final product 3 and Na(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 experimental data. A and B are adducts of a mesitoyl phosphaketene molecule with one and two (OCP)− ions, respectively. This indirectly indicates the initial formation of mesitoyl phosphaketene, MesCO−P=C==O. The common structural motif of A and B is the four-membered P(CO)2P ring, which was first described for [O2C−P(CO)3P]3−, the adduct of a CO2 molecule and two (OCP)− ions.16 The 31P-NMR chemical shifts of this adduct (δ = 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 bismesitoyl phosphide [P(COMes)2]− (δ = 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 Na(OCP) in the hope of identifying another possible intermediate. When Na(OCP) and 4 were reacted at −78 °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 mesitoyl 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 oxadi-phosphole 3. We assume that in the last step a mesitoyl chloride...
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 (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 (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 (OCP)$^-$ anion and B (vide supra).38 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 $-35$ °C using $^{31}$P-NMR spectroscopy and the concentrations of Na(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 (OCP)$^-$ is slower than the subsequent reaction of the activated acyl phosphaketene MesCO–P=C=O IM1 with another equivalent of (OCP)$^-$ ion. Indeed, this reaction between IM1 and (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 (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

![Scheme 3 Proposed reaction mechanism leading to 3.](image-url)
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, \( k_{A} \). 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 (\( k_{B} \) is similar to \( k_{A} \)) 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. 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 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 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. 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 orbitals (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) plot \( 31 \) (Fig. 8c), which shows a disconnection in the topology of the delocalized electrons. Similarly, the fragmentation of 3-azidoacrylaldehyde to isoxazol and dinitrogen has been described and classified as a pseudo-coarctate process.

**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 \( 31 \)P-NMR spectroscopy, kinetic measurements and theoretical calculations. Several \( [2 + 2] \) cycloaddition products were observed as intermediates using \( 31 \)P NMR spectroscopy and identified with the help of chemical shift calculations, which demonstrate the performance 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.

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of these theoretical methods. The formation of another, not yet observed, intermediate was made plausible through the reaction of Na(OCP) with a thiaoacryl chloride which gave a stable sodium 1,2,4-thiadiphosphol-3-olate. As observed previously in reactions with isocyanates and carbon dioxide, a remarkable feature in the reactions between (OCP)$^-$ salts and heterocumulenes is the equilibrium, $X=YZ+{(OCP)^-\Rightarrow [XY(PCO)Z]^-,}$ 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 $\alpha,\beta$-unsaturated organic azides and indicates a possible resemblance between the isovalence electronic (OCP)$^-$ and (N$_3$)$^-$ anions.

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Based on $^{31}$P-NMR spectroscopic investigations, clean reactions were observed with other aromatic acyl chlorides (e.g. o-toluoyl chloride, 2,6-difluorobenzoyl chloride). Reactions with aliphatic acyl chlorides, however, led to the formation of 1,2,4-oxadiphospholes in small amounts and a number of unidentified by-products were detected.


23 The NICS(0) value for 3’ bearing methyl instead of mesityl groups is –9.9 ppm at the B3LYP/6-311+G** level of theory. The replacement of the ester function with a hydrogen results in a NICS(0) value of –10.8 ppm.


28 Two (OCP)$^–$ anions and a CO$_2$ molecule reversibly form the four-membered ring [O$_2$C–P(CO)$_2$P]$^–$. According to the reported mechanism, initially the phosphaketene [O$_2$C–P=C=O]$^–$ is formed, which is then attacked by another (OCP)$^–$ anion. This is followed by an intermolecular nucleophilic ring closure, see ref. 11c. The formation of A and B is expected to proceed in a similar way.


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