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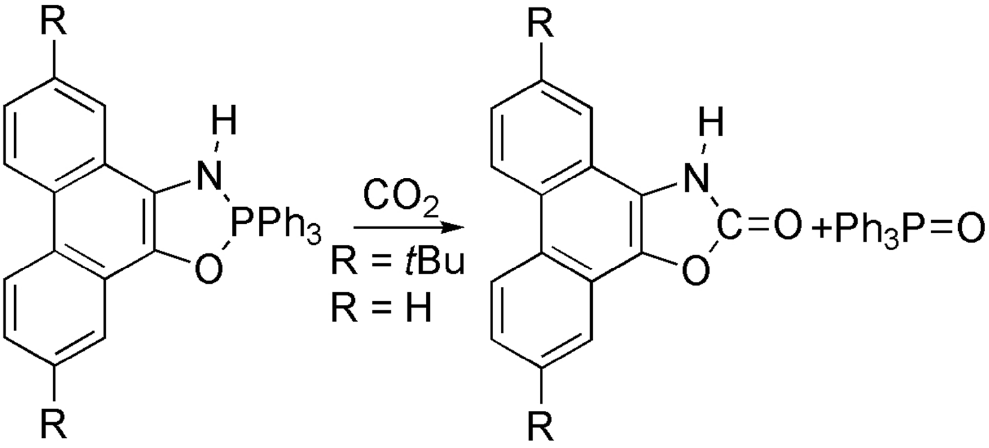

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ARTICLE TYPE

Carbon dioxide as a primary oxidant and a C1 building block†

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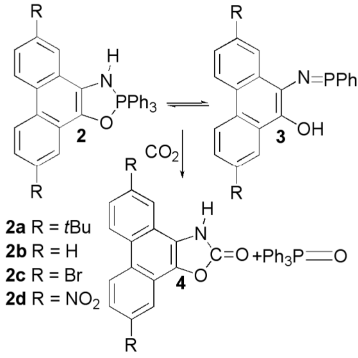
2,3-Dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2-λ^5-oxazaphospholes react with carbon dioxide in an overall second order reaction at room temperature to 3*H*-phenanthro[9,10-d]oxazol-2-ones and triphenylphosphine oxide in good yields. Nucleophilic attack of the phenolate on CO_2 and formation of $Ph_3P{=}O$ was found.

Carbon dioxide chemistry (in particular, capture and conversion) has attracted much attention from the scientific community due to global warming associated with positive carbon accumulation.[1] The most widely used chemical absorption technique for carbon capture and storage/sequestation would be essentially adopting amino-containing absorbents through formation of C–N bond in terms of mechanistic consideration.[2] However, extensive energy input in desorption and compression process would be a crucial barrier to realize it practically. On the other hand, CO_2 is very attractive as an environmentally friendly feedstock to replace the hazardous phosgene route for making commodity chemicals, fuels, and materials from a standpoint of green chemistry, whereas the reactions involving CO_2 are commonly carried out at high pressure, which may not be economically suitable and also pose safety concerns. The challenge is to develop catalysts that are capable of activating CO_2 under low pressure (preferably at 1 bar), and thus incorporating CO_2 into organic molecules catalytically or find new energy-rich reagents for these reactions.[3] If we confine ourselves to reactions of CO_2 with *N*- or *O*-nucleophiles these include mainly compounds such as ammonia,[4] amines,[5] azides,[6] aziridines,[7] inorganic oxides,[8] a terminal P=O,[9] alcohols[10] and other various terminal oxide anions.[11] With aziridines carbon dioxide react to give oxazolidinones[12] or polyurethanes in the presence of a catalyst and the latter in its absence. However, in both cases elevated CO_2 pressures and higher temperatures are required. Oxazolidinones can also be prepared from propalgylalcohol and amines in ionic liquid at 25 bar CO_2 pressure and CuCl as catalyst.[13] Quinazolinediones are formed from aminobenzonitriles in excellent yields in water.[14] CO_2 would be a good and abundant C1 source for chemistry and its elimination from the atmosphere very desirable. Its reactions to valuable compounds are very limited, especially in industrial context, due to its low reactivity on the one side, and otherwise its high concentration in the atmosphere, which poses big environmental problems.

1,2-Quinones react with tertiary phosphines in a [4+1] electrocyclic reaction giving dioxaphosphole heterocyclic rings.[15] Monoimines of 1,2-quinones (**1a-d**) give 1,3,2-oxazaphospholes (2) by the use of tertiary phosphines in good yields.[16] Where the monoimines are unstable they can also be prepared from the corresponding quinones and triphenylphosphine in a sealed tube under ammonia. Electron-releasing groups on the quinones make the nucleophilic replacement of the C=O bond with NH_3 to a C=NH functionality difficult or impossible (*e.g.* R = NMe_2, OR).

1,3,2-Oxazaphospholes exhibit tautomerism as shown in Scheme 1 between the oxazaphosphole form (**2**) and the imino phosphorane form (**3**) dependent on the consistency or the solvent of solution (Scheme 1).[17] Oxazaphospholes (**2**) seem to be stable in the solid form. In solution, however the tautomeric compounds of the iminophosphorane form (**3**) are also present. ^{31}P NMR spectra in the range of 39-51 ppm are characteristic for **2** and those of the form **3** have a shift in the range from -23 to -8 ppm. In more basic solvents the oxazaphosphole form **2** is dominant. In solution they decompose readily in air due to dioxygen or moisture.



Scheme 1 The tautomeric forms of 1,3,2-oxazaphospholes and their reaction with CO_2.

2,3-Dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ^5-oxazaphospholes (**2a,b**) react with carbon dioxide in acetonitrile at room temperature slowly (24 h) and at reflux temperature in a fast reaction (2 h) to give 3*H*-phenanthro[9,10-d]oxazol-2-one (**4a,b**) in 78-85% yields (Scheme 1). The same reaction products can be obtained when the corresponding 9,10-phenanthrenequinone monoimines are used with a stoichiometric amount of triphenylphosphine and CO_2. The endproducts crystallise from the solution and Ph_3PO can be obtained from the filtrate purified by column chromatography using methanol as eluent. X-ray structure determination of **4b** secured the structure with bond distances of C=O 1.196(7), C-N 1.378(8), and C-O

1.374(7) Å comparable to those found in similar molecules (Fig. 1).[18] The other product formed (38%), compared with an authentic sample, was found to be triphenylphosphine oxide with ν(P=O) at 1191 cm^{-1} in the FTIR spectrum[19] and a signal at 25.5 ppm in the ^{31}P NMR spectrum.[20]

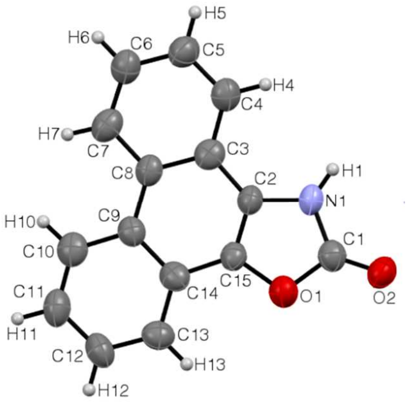


Fig. 1 X-ray crystal structure of 3*H*-phenanthro[9,10-d]oxazol-2-one (**4b**). Red O, blue N, black C, white H. Selected bond distances (Å) and angles (°): C1-O2 1.196(7), C1-O1 1.374(7), C1-N1 1.378(8), C2-C15 1.350(8), C2-N1 1.391(7), C15-O1 1.402(7), O2-C1-O1 125.0(6), O2-C1-N1129.0(6), O1-C1-N1 106.1(6), C15-C2-N1 106.0(6), N1-C2-C3 131.3(6), C2-C15-O1 109.4(5).

Kinetic measurements under pseudo first order condition (constant CO_2 concentration, 1 bar) (Fig. 2) and with different 1,3,2-oxazaphosphole concentrations resulted in a second order overall rate equation (1).

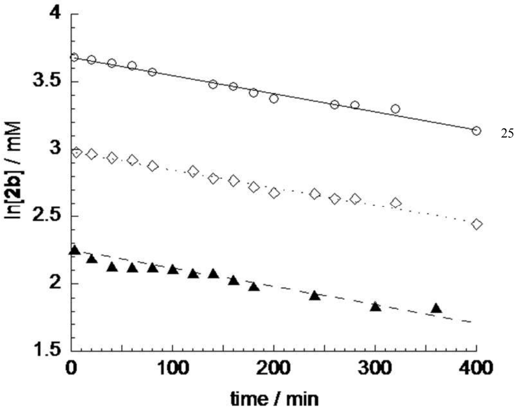


Fig. 2 Time courses of the reactions of the initial 2,3-dihydro-2,2,2-triphenyl phenanthro[9,10-d]-1,3,2λ^5-oxazaphosphole (**2b**) concentration with CO_2. [**2b**]$_o$ = 40 mM (○), 20 mM (◇), 10 mM (▲) by 1 bar of CO_2 pressure.

$$\text{Reaction rate} = k_2\,[\text{1,3,2-oxazaphosphole}][CO_2] \tag{1}$$

The 2,7-dinitro and 2,7-dibromo derivatives (**2c,d**) did not react with CO_2. However, the 2,7-di-*tert*-butyl derivative **2a** resulted in a faster reaction to give **4a**. Probably the nucleophilic power of their deprotonated forms of the iminophosphoranes (**5c,d**) do not reach the energy level necessary for the reaction ($E°_{1/2}$ = 213 and 351 mV respectively *vs* Fc/Fc$^+$). The elevated rate of the latter reaction is based on the enhanced nucleophilic character of the *O*-nucleophile formed by deprotonation of **3a** due to the two *tert*-butyl electron-releasing groups. The addition of stoichiometric amount of triethylamine to the reaction mixture resulted also in faster reaction rate as a result of higher depronation of **3b** (k_2 = 6.81±0.12 and k_2^{Et3N} = 28.69±2.42 M^{-1}s^{-1}). According to literature data iminophosphoranes do not react with carbon dioxide.[21] However, phenolates[22] and also carbanions[23] are potent nucleophiles. They react even with triplet dioxygen when their electron affinity lies below 20 kcal mol^{-1}.[24] That is in agreement mostly with those of the nucleophilic reactions on CO_2.

Reaction of **3b** with $C^{18}O_2$ (~50:50 $C^{16}O_2$: $C^{18}O_2$) under similar conditions revealed that the carbonyl *O*-atom of **4b** and the *O*-atom of triphenylphosphine oxide originates from the labeled $C^{18}O_2$. The ^{18}O:^{16}O ratio in both products based on GC-MS measurements are in a ratio of 45:55 and 43:57 respectively. The reaction product triphenylphosphine oxide have been identified by FTIR spectroscopy with the help of its ν(P=O) streching frequencies of 1184 and 1152 cm^{-1}, Δν = 32 cm^{-1} (calculated for P=^{18}O 1184 cm^{-1}, Δν = 32 cm^{-1}), (P=^{16}O and P=^{18}O), 25.5 ppm in the ^{31}P NMR spectrum. Mass spectrometric analysis of the reaction product indicated a molecular formula $C_{18}H_{15}{}^{16}OP$ (*m/z* [M]$^+$: 278.28 and 280.28) for $Ph_3P{=}^{16}O$ and $Ph_3P{=}^{18}O$. 3*H*-Phenanthro[9,10-d]oxazol-2-one (**4b**) showed in FTIR ν(C=^{16}O and C=^{18}O) 1752 and 1726 cm^{-1}, Δν = 26 cm^{-1} (calculated for C=^{18}O 1726 cm^{-1}, Δν = 26 cm^{-1}) and mass spectroscopic data of the molecular formula $C_{15}H_9N^{16}O_2$ (*m/z* [M]$^+$: 235.24 and 237.24) for the ^{16}O- and ^{18}O-derivative (Fig. 3).

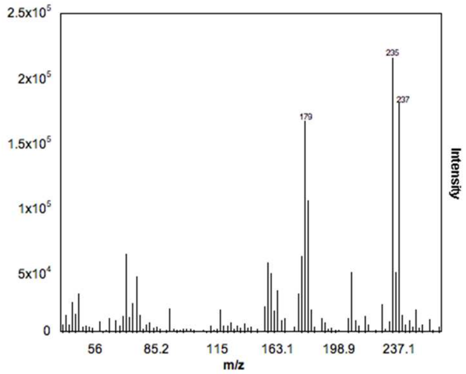
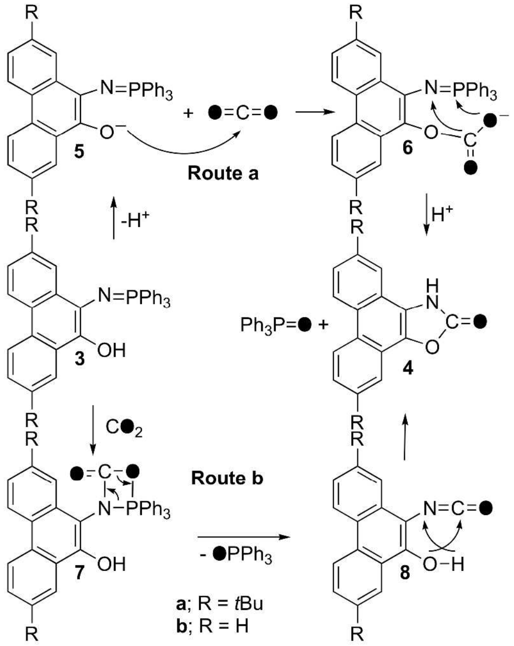


Fig. 3 The GC-MS spectrum of the reaction product of 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ^5-oxazaphosphole (**4b**) prepared with a ~50:50 mixture of $C^{16}O_2$:$C^{18}O_2$ at room temperature in acetontrile.

The mechanism of the reaction (Scheme 2) can be interpreted as a nucleophilic attack of the deprotonated iminophosphorane (**5**) on the carbon atom of CO_2 yielding a deprotonated semiester of carbonic acid **6**, from which then the N=P bond of the iminophosphorane part of the molecule abstracts an oxygen atom to form triphenylphosphine oxide and the carbon atom of the O=C=O part closes with the imino *N*-atom of **6** to give the oxazol-2-one ring system **4a,b** as endproduct (**Route a**). **Route b**, which is also in agreement with the kinetic data, is practically an aza-Wittig reaction.[21] The iminophosphorane tautomer form **3** reacts with CO_2 forming the four-membered ring compound **7**[25], which decomposes to triphenylphosphine oxide and the isocyanate **8**. This is followed with the intramolecular reaction of the isocyanate and the phenolic OH to end up in the oxazol-2-one (**4**). Both pathways may be operative, however the faster reaction rate when NEt_3 is added seems to support **Route a** and no reaction of iminophosphranes (**3**) with CO_2 to form a four-membered ring is known from the literature. Recent results demonstrating a nucleophilic attack of an oxo anion are in agreement of this assumption.[11]



Scheme 2 Possible mechanism of CO_2 fixation.

Kinetic investigations resulted in an overall second-order rate equation with k_2 value of 6.81±0.12 $M^{-1}s^{-1}$. Due to the large activation energy (92 $kJmol^{-1}$) and the negative activation of entropy (-21 $Jmol^{-1}K^{-1}$) we can conclude that the rate-determining step involves a nucleophilic addition of the phenolate **5b** on the carbon atom of CO_2 or the formation of the four-membered ring **7**. Labeling experiments straitforward support that the *O*-atom of triphenylphosphine oxide and that of the carbonyl group originates from carbon dioxide.

Conclusions

In summary, we have disclosed that carbon dioxide, having the most oxidized state of carbon, the biggest obstacle for its implementation in industrial processes as a raw material in its low energy level, acts as a primary oxidant and as a C1-building block. We have found that 1,3,2-oxazaphospholes react easily with carbon dioxide even at room temperature to oxazol-2-ones and triphenylphosphine oxide. This methodology serves as a useful alternative for the photochemical preparation of oxazol-2-ones starting from benzoin.[25] In a coupled reaction triphenylphosphine is oxygenated to its oxide. The *O*-atoms of oxazol-2-ones and Ph_3PO originates from CO_2 proved by labeling experiments, and assumedly in a similar fashion like the Wittig reaction[26] this is the driving force for the reaction. 1,3,2-Oxazaphospholes should be rich on energy and we believe that the deprotonated form of the iminophosphorane tautomer **3** attacks the carbon dioxide in a nucleophil manner. This argumentation opens a new type of energy rich phenolate nucleophiles which are able to react with CO_2 in negative Gibbs free energy reactions.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental details of synthesis and structural characterisation, kinetics, electrochemical and spectroscopic data. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

‡Crystallographic data for **4b**: $C_{60}H_{36}N_4O_8$; M_r = 940.93; crystal size 0.14 × 0.06 × 0.02 mm^3; monoclinic; C2/c; a = 41.056(1), b = 10.5170(5), c = 22.3769(9) Å; β = 118.092(2)° ; V = 8523.8(6) $Å^3$; Z = 8; ρ_{cald} = 1.466 g cm^{-1}; μ = 0.099 mm^{-1}; $F(000)$ = 3904; T = 203(2)K; Kappa CCD area detector equipped with monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) ; 7254 reflections measured (Θ_{max} = 0.998°); 2499 independent reflexions; R_1 = 0.0865; wR_2 = 0.2074; GOF = 0.961. CCDC 956401 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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