Electrifying P(V): Access to Polar and Radical Reactivity

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Abstract: Electrochemical, fully stereoselective P(V)-radical hydrophosphorylation of olefins and carbonyl compounds using a P(V) reagent is disclosed. By strategically selecting the anode material, radical reactivity is accessible for alkene hydrophosphorylation whereas a polar pathway operates for ketone hydrophosphorylation. The mechanistic intricacies of these chemoselective transformations were explored in-depth.

Aside from life itself, phosphorus-containing compounds play crucial roles in organic synthesis, medicinal chemistry, oligonucleotide therapeutics, and materials chemistry [1]. Due to their significance, there has been a strong focus on the development of new phosphorylation reagents and methods with particular interest in P—C bond formation over the past several decades (Figure 1A). The formation of P—C bonds, specifically in phosphonates, has garnered significant attention in medicinal chemistry due to their chemical and enzymatic stability.[2] Research has demonstrated that phosphonates can mimic various functional groups, such as amides, sulfoxides, sulfones, and sulfides.[3] The isosteric replacement of an P—O bond with a P—S bond (referred to as the "thio-effect") has been shown to confer additional resistance to metabolism and, in certain instances, an increase in efficacy.[4] The PSI-reagent platform, which is based on the P(V) oxidation state, is a useful tool for practically applying and utilizing the thio-effect (Figure 1B).[5] The PSI-platform (P(V) phosphorylation reagents) is inherently modular, comprising an initial "loading" step where phosphorus is introduced followed by a "coupling" step whereby a nucleophile is added, releasing the final P-based functional group. In its initial manifestation, various nucleophiles, such as alcohols[6], amines[7], and Grignard and organolithium reagents [8] were utilized (guided by 2-electron logic to access P-heteroatom bonds). Shortly thereafter, the platform was further developed to add to unsaturated systems via P-centered radicals (1-electron logic) to gain access to phosphonate bonds (P—C).[9] In that work, fully stereo- and chemoselective P(V)-radical hydrophosphorylation using Azobisisobutyronitrile (AIBN) as a radical chain initiator was reported in contrast to methods involving metal catalysis and toxic reagents like selenium, wherein stereocontrol and chemoselectivity were low and for which further derivatization is not an option.[2a, 10] This Communication discloses the first practical electrochemical, stereocontrolled, and chemoselective method for radical transformations of P(V) through electrochemical initiation without using radical initiators such as AIBN (Figure 1C). This approach allows for phosphorylation reactions (of both C=C and C=O bonds) to be carried out in a mild, rapid, and safe manner.

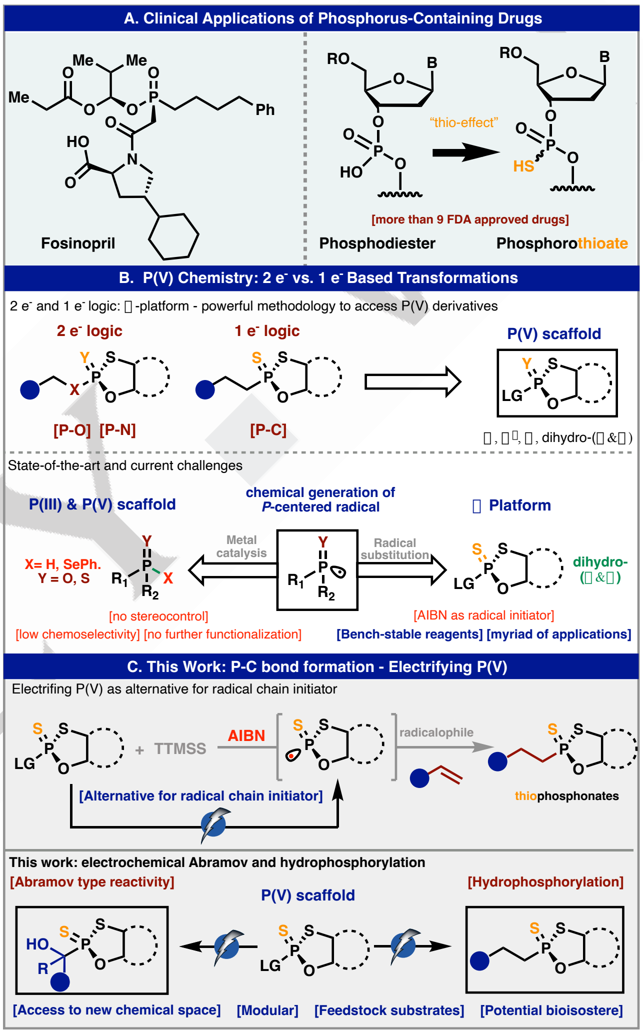
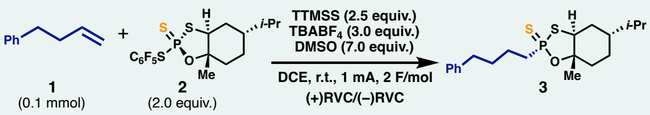


Figure 1. (A) clinical application for phosphorus-containing drugs **(B)** P(V) Chemistry: 2 e- vs. 1 e- Based Transformations allow access to P(V) derivatives. **(C)** Electrifying P(V) as alternative for radical chain initiator and unlocking new chemical space

Prior studies from this lab accessed P(V)-centered radical reactivity by heating reagent **2** at 50 °C for >8 hours to ensure a slow decomposition of AIBN and increase the diastereomeric outcome of P—C bond formation. It was reasoned that P-centered radicals might be accessible under more industrially favorable conditions without the use of AIBN due to its relatively lower thermal stability and limitation for use on scale.[11] A particularly promising alternative to the use of chemical radical chain initiators is electrochemical initiation, inspired by extensive research in electrochemical polymerization [12], which has proven to be a viable substitute for traditional polymerization techniques.

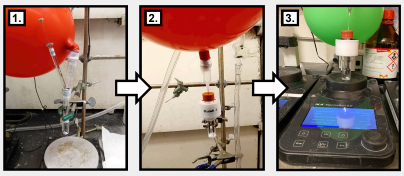
Optimization on Alkene and Carbonyl Hydrophosphorylation

(A) Optimization on Hydrophosphorylation



[Chemoselective] [Stereoselective] [Unactivated alkenes]

Entry	Deviation from above	NMR yield [%]	d.r.
1[a]	none	86 (81 isol.)	20:1
2	ACN, no DMSO	35	10:1
3	DMSO	0	-
4	(+)Zn/(-)RVC, 5 mA, DMF	15	5:1
5	(+)Mg/(-)RVC, 5 mA	0	-
6	no electricity	0	-
7	no TTMSS	0	-
8	0.5 mA (≈12 h)	86	20:1
9	$TBABF_4$ (1 equiv.)	70	17:1
10	(+)Zn/(-)RVC, 5 mA	75	4.5:1
11	(+)RVC/(-)Zn, 5 mA	80	12:1



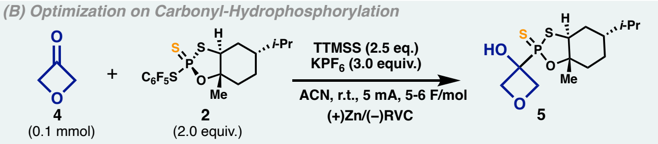
Standard procedure

1. Dissolve alkene, Π, TTMSS, $TBABF_4$ and DMSO in DCE.

2. Transfer into electrasyn Vial.

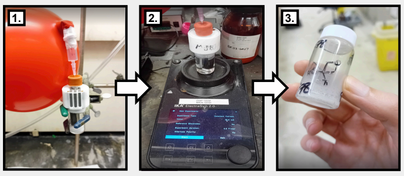
3. Electrolyze under argon

(B) Optimization on Carbonyl-Hydrophosphorylation



[Access to new chemical species] [No stereoinversion on Phosphorus] [Scalable]

Entry	Deviation from above	NMR yield [%]
1[b]	none	95 (70 isol.)
2[c]	(+)Zn/(-)RVC, 15 mA	>95
3	(+)RVC/(-)RVC	8
4	(+)Mg/(-)RVC	trace
5	TFA	0
6	Ph_3SiH	0
7	no electricity	0
8	no TTMSS	0
9	(1 equiv.) Π, (1 equiv.) TTMSS	12
10	(1 equiv.) TTMSS	0
11	(1 equiv.) Π	39



Batch scale-up

[0.7 mmol]

TTMSS (2.5 equiv.)
KPF_6 (3.0 equiv.),
ACN, r.t., 35 mA, 6 F/mol
(+)Zn/(–)RVC

yield: 55%

Table 1. (A) Optimization of alkene hydrophosphorylation. **(B)** Optimization of carbonyl hydrophosphorylation. Yields determined by ^{31}P NMR with triphenyl phosphate as an internal standard.

The invention of a direct electrochemical hydrophosphorylation was initially explored with 4-phenyl-1-butene (**1**) and dihydro-Π reagent (**2**). Although other P(V) reagents were considered, **2**, which was previously optimized and customized for P-centered radical type reactivity, was chosen for this study (Table 1A). In its fully optimized form, electrochemical hydrophosphorylation is relatively simple and convenient to conduct under argon in an undivided cell. To a mixture of dihydro-Π (**2**) (2.0 equiv.) and Tetrabutylammonium tetrafluoroborate ($TBABF_4$) (3.0 equiv.) were added a stirred solution of Tris(trimethylsilyl)silane (TTMSS) (2.5 equiv.) and DMSO (7.0 equiv.) in 1,2-Dichloroethane (DCE) (0.033M). Electrolysis at room temperature for 6 h delivered **3** in 81% isolated yield as a single diastereomer (d.r. >20:1, entry 1). It was found that replacing the solvent with acetonitrile lowered the yield and reduced the d.r. (entry 2), and no product was obtained while replacing the solvent with DMSO (entry 3). Next, various electrochemical parameters were explored. It was found that (+)Zn/(–)RVC in DMF gives relatively low yield (entry 4) and that using (+)Mg as an anode ablated hydrophosphorylation reactivity (entry 5). The role of DMSO in the optimized conditions is to further solubilize the electrolyte (i.e. lowering the resistance) and to serve as a source of electrons to balance the reductive fragmentation of dihydro-Π (**2**) (see mechanistic discussion below). Not surprisingly, rudimentary control studies (entries 6-7) demonstrated the need of TTMSS and electricity for efficient radical chain processes. Lowering the current to 0.5 mA furnishes the hydrophosphorylation products in slightly diminished yield (entry 8) and finally it was found that lowering the electrolyte equivalents to 1.0 equiv (instead of 3.0 equiv) form the product in lower yield and d.r. (entry 9) (for more details see SI). Interestingly, similar reactivity can be achieved using either (+)Zn/(–)RVC or (+)RVC/(–)Zn electrodes albeit with lower d.r. (entries 10-11). This observation indicated that the reaction could proceed under both reductive and oxidative conditions. In numerous experiments during the optimization phase, the formation of H-Phosphonate (**36**) (Fig. 2A) was observed as the main side product (see SI)). Thus, further investigation of the reactivity of this P—nucleophile was pursued to achieve addition across C=O bonds since "*Abramov*" type reactivity generally requires strong bases for nucleophilic phosphorylation (Table 1B).[13]

Systematic optimization for such a nucleophilic addition was conducted using **2** and 3-oxetanone. In its fully optimized form, 1,2-phosphorylation is straightforward and convenient to conduct under argon in an undivided cell. To a mixture of dihydro-Π (**2**) (2.0 equiv.) and KPF_6 (3.0 equiv.) were added a stirred solution of TTMSS (2.5 equiv.) and ketone (1.0 equiv.) in Acetonitrile (ACN) (0.033M) followed by a subsequent electrolysis at room temperature for 4-5 h resulting in a 70% isolated yield of adduct **5** (entry 1). It was found that the reaction is not sensitive to current density (15 mA) which can reduce the reaction time to 1 h (entry 2) although a lower current density was chosen for the final conditions due to chemoselectivity concerns. Changing the electrode parameters to (+)RVC/(–)RVC and (+)Mg/(–)RVC dramatically reduces the reactivity (entries 3-4). Addition of Trifluoroacetic acid (TFA) (entry 5) as proton source or replacement of TTMSS with Ph_3SiH (entry 6) shut down the reaction. Control studies (entries 7-8) demonstrated the need of TTMSS and electricity. Lastly it was found that the ratio between P(V) reagent (**2**) and TTMSS are essential to obtain the product in high yields (entries 9-11)

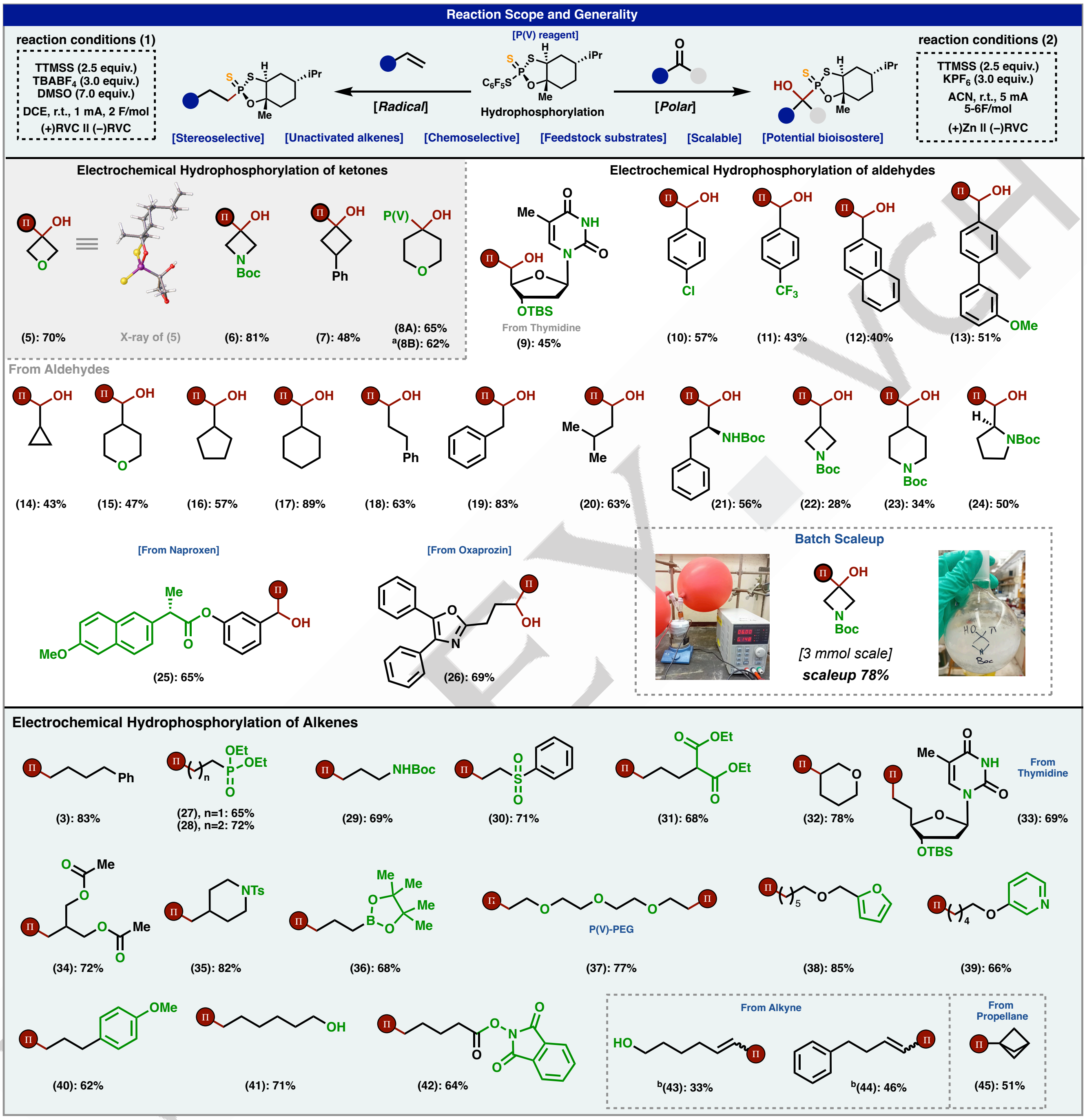


Table . 2: Reaction scope and generality for electrochemical thio-phosphorylation reactivity. a, 8B was formed from Ψ. b, compounds was isolated as E/Z mixture.

With a robust set of optimized conditions in hand for these two transformations, the substrate scope was explored as depicted in Table 2. The 1,2-phosphorylation conditions were found to be general for ketones bearing several different substituents including ethers (**5** and **8**, 70% and 65% respectively), protected amines (**6**, 81%), and strained ketones (**5-7**, 48-81%). Although adducts **5-8** were obtained in relatively high yields, decomposition back to the parent ketone was observed during workup which explains the difference between the ^{31}P NMR and isolated yields (see SI). Dihydro-Ψ, another member of P(V) reagents, was also compatible in carbonyl hydrophosphorylation conditions (**8b**) (see SI). Various categories of aldehydes (**9-24**) were also explored in this study, including benzylic aldehydes (**10-13**), unconjugated aldehydes with a variety of ring sizes (**14-24**), and α-heteroatom-substituted aldehydes (**21**, **24**, and **9**). The relatively high functional group tolerance suggests that this methodology could also be applied to substrates of biological interest, such as nucleotide bioisosteres (**9**) and amino acid bioisosteres (**19-21** and **24**) in preparatively useful yields (28-89%).

Finally, we applied the carbonyl hydrophosphorylation to drug like scaffold, Naproxene derivative (**25**, 65%) and Oxaprozine derivative (**26**, 69%). As alluded to above, the main limitation of this reaction is the stability of the products themselves as many ketone and aldehyde substrates (see SI) simply revert back to starting material upon workup and purification. Attempts to further derivatize the adducts using DBU and a nucleophile similarly led to ketone. Importantly, although the stereochemical result at P was completely controlled, the diastereoselectivity at C of the adducts was generally not (usually *ca.* 1:1). It was found that the electrochemical hydrophosphorylation is scalable using IKA (0.7 mmol) and customized (3 mmol) systems (Table. 1 and Table. 2). The scope of stereocontrolled alkene hydrothiophosphorylation was also investigated, as outlined at the bottom of Table 2. A variety of unactivated alkenes provided products with yields ranging from 65% to 83%, exhibiting excellent diastereoselectivity (at P). The mild conditions facilitated high chemoselectivity, with functional groups such as phosphonates being well-tolerated, resulting in bisphosphonate products (**27-28**) in high yields (65% and 72%). Compounds containing protected amines also showed high compatibility with the method (**29,** 69%) and (**35,** 82%). Additionally, alkenes with electron-withdrawing groups are also accommodated (**30,** 71%). Functional groups that are typically challenging in transition metal-catalyzed reactions, such as Bpin (**36,** 68%), were also well-tolerated. Moreover, medicinally relevant functionalities, including nucleosides and phosphorylated-PEG (Polyethylene glycol) derivatives (**33** and **37**) were investigated and isolated in good yields (69% and 77%). It was found that the reaction condition Is compatible with esters (**34**, 72%) and alcohols (**41**, 66%). Additionally, the mild electrochemical conditions enabled electron-rich heterocycles (**38**) and arenes (**40**) to yield hydro-phosphorylated products in good to high yields (85% and 62%), which are typically challenging moieties under oxidative electrochemical conditions.

Interestingly, the redox-active ester (**42**) was well-tolerated with 64% isolated yield. Other radicalophiles were investigated and applied to the electrochemical hydrophosphorylation such as alkyne (**43** and **44**) and propellane (**45**).

In a comparison between electrochemical and thermal hydrophosphorylation, olefins conjugated with arenes performed significantly better under AIBN-initiated conditions than with the electrochemical method (see SI).

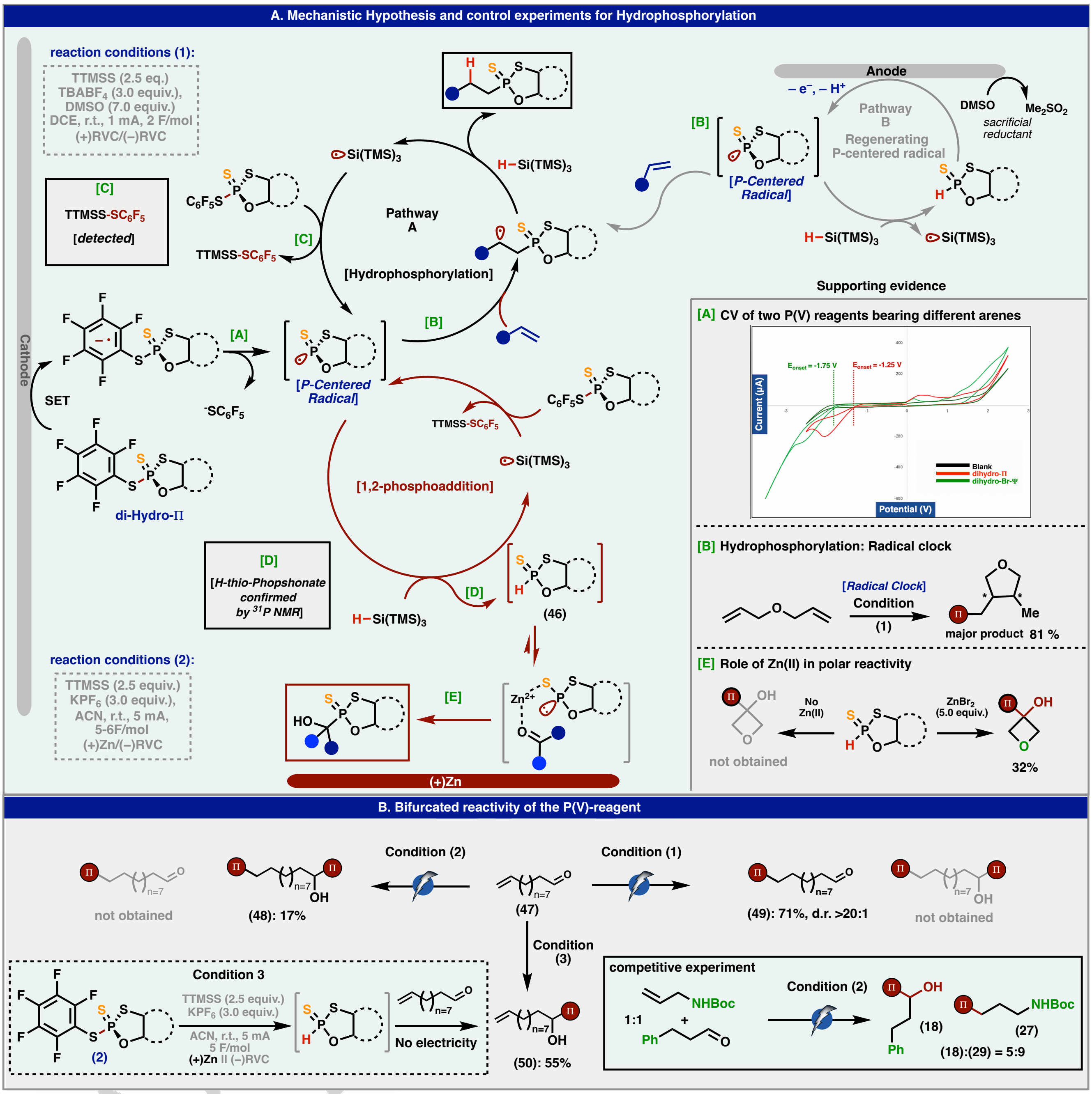


Figure 2. (A) Mechanistic studies and supporting evidence for polar and radical hydrophosphorylation of alkene and carbonyl. (B) hydrophosphorylation chemo-selectivity for mono functionalization

The most interesting aspect of this study is the bifurcated reactivity of the P(V)-reagents that can be modulated mainly by changing the anode employed. A mechanistic picture and supporting experiments to explain the unique reactivity exhibited in both olefin and carbonyl hydrophosphorylation is illustrated in Figure 2. The key role of the pentafluorothiophenol as leaving group is demonstrated by its reduction potential (-1.35 V) as compared to di-Hydro-Br-Ψ (see panel [A] for CV). The electron-deficient nature of the arene enables the unveiling of the P-centered radical presumably via dissociative electron transfer at an accessible reduction range.[14] Formation of a P-centered radical is supported by radical clock experiments (panel [B]). We propose that the *olefin hydrophosphorylation* product is formed from the P-centered radical via two major pathways. The first pathway is a direct addition of the P-centered radical onto the alkene, generating a C-centered radical. A subsequent HAT with TTMMSS furnishes the thiophosphonate product and a silyl radical which can close the chain propagation cycle via abstraction of pentafluorothiophenol from dihydro-Π; (TMS)$_3$Si-SC$_6$F$_5$ which was detected by ^{19}F NMR and LC-MS analysis (panel [C], see SI for more details). The second mechanistic pathway leading to the same product can occur when the P-centered radical undergoes HAT to generate H-phosphonate (**46**) (see panel [D]). It is in this step that added DMSO can assist in completing the electrolytic cycle as a sacrificial reductant.[15] The P-centered radical can be regenerated as well from **46** via anodic oxidation when a non-sacrificial anode is employed (Pathway B). In either case, formation of **46** was observed as a side product and in the absence of a radical acceptor, it was the major product. In the case of *carbonyl phosphorylation* (Abramov reactivity) formation of **46** is again invoked as above. We postulate that this species adds to carbonyl compounds non-electrochemically in the presence of Zn(II) salts released from the sacrificial anode.[16] To test this hypothesis, non-electrochemical experiments were performed; **46** underwent carbonyl hydrophosphorylation in the presence of $ZnBr_2$ whereas no product was observed in its absence (panel [E]). Finaly it was found that consistent electrical current is crucial to maintain both electrolytic and parallel chemical pathways (see SI section 6.6)

The lessons from this mechanistic study could be used to "dial-in" a desired reactivity profile on substrates bearing both an olefin and a carbonyl group. Thus, exposure of undecanal (**47**) to reaction condition 1 led exclusively to the olefin hydrophosphorylation product (**49**). Submitting (**38)** to reaction condition 2 delivered modest yield of the diphosphorylated adduct (**48**). A third set of reaction conditions involved pre-electrolysis of reagent (**2**), terminating the electrolysis, followed by addition of (**47**) to cleanly afford only carbonyl hydrophosphorylation product (**50**).

To summarize, this study lays a foundation to understand the reactivity of P(V)-based reagents under electrolytic conditions to avoid the use of chemical radical initiation. Two distinct methods for the hydrophosphorylation of olefins (conditions 1) and carbonyl groups (conditions 2) have been devised by strategically choosing the anode material. The former reaction appears to lie solely in the realm of radical reactivity whereas the latter relies on a polar pathway. This study represents a rare example of forging P–C bonds commencing with the P(V) oxidation state in contrast to conventional approaches that begin with P(III)-based reagents. The scope of these transformations is broad as a consequence of the high chemoselectivity. Mechanistic studies explain the basis for this bifurcated reactivity which can be employed to achieve either transformation on polyfunctional substrate.

Acknowledgements

Financial support for this work was provided by the NSF Center for Synthetic Organic Electrochemistry (CHE-2002158). M. N. thanks the Council for Higher Education and Fulbright Israel. We are grateful to Dr. G. J. Kroon and Dr. L. Pasternack (Scripps Research) for NMR spectroscopic assistance; Dr. M. Gembicky and Dr. J. B. Baliley for X-ray crystallographic analysis.; Dr. M. Costantini, A. Rerick, P. Neigenfind, N. Nasiri and A. Pollatos for helpful discussions (Scripps Research).

Keywords: Thiophosphate • Electrochemistry• Radical Reaction• Abramov• P(V) • PSI.

Author Contributions

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