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A Systems Approach to a One-Pot Electrochemical Wittig Olefination Avoiding the Use of Chemical Reductant or Sacrificial Electrode

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Abstract: An unprecedented one-pot fully electrochemically driven Wittig olefination reaction system without employing a chemical reductant or sacrificial electrode material to regenerate triphenylphosphine (TPP) from triphenylphosphine oxide (TPPO) and base-free in situ formation of Wittig ylides, is reported. Starting from TPPO, the initial step of the phosphoryl P=O bond activation proceeds through alkylation with RX (R = Me, Et; $X = OSO_2CF_3$ (OTf), affording the corresponding $[Ph_3POR]^+ X^-$ salts which undergo efficient electroreduction to TPP in the presence of a sub-stoichiometric amount of the Sc(OTf)₃ Lewis acid on a Ag-electrode. Subsequent alkylyation of TPP affords Ph_3PR^+ which enables a facile and efficient electrochemical in situ formation of the corresponding Wittig ylide under base-free condition and their direct use for the olefination of various carbonyl compounds. The mechanism and, in particular, the intriguing role of Sc^{3+} as mediator in the TPPO electroreduction been uncovered by Density Functional Theory calculations.

The Wittig olefination reaction (WOR) is one of the most common synthetic routes to produce functional alkenes.^[1] The perhaps most prominent case of WOR at industrial scale is the production of vitamin A.^[2] The latter affords a stoichiometric amount of triphenylphophine oxide (TPPO) resulting as a byproduct in several tons per year during the synthesis (Scheme 1a). Henceforth, reduction of organophosphine oxides to the corresponding phosphine (e.g., Ph₃P, TPP) is not only of fundamental but also of utmost industrial interest.^[3] In addition, the complete removal of TPPO from reaction mixtures is often not straightforward.^[4] Until now, deoxygenation to regenerate TPP can nearly exclusively be achieved using chemical reductant e.g., silanes,^[3b, 5] boranes^[3a, 6] and aluminum (hydrides)^[7] and therefore, the pursuit of other reducing agents^[8] or regeneration processes has gained attention in the last few years (Scheme 1a).^[3a, 3b] Because regenerating TPP with expensive reduction agents is not a viable solution, alternative approaches have been tested.^[9] Among them, electrochemical reduction of TPPO to TPP is a highly attractive aim, but remains cumbersome.^[10] Up to now, electroreduction of TPPO to TPP suffers from shortcomings that prevent from its recycling on a commercially feasible scale.[11]

Previous attempts towards selective electroreductive deoxygenation of TPPO remained unsatisfacory due to undesired C-P bond dissociation to $Ph_2P(O)H$ and benzene.^[10] The most promising approaches towards successful TPP regeneration from

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 Supporting information for this article is available on the WWW under http:// TPPO proceed via activation of the P=O bond with Lewis acids (LA) such as Me₃SiCl^[11a, 11b], AlCl₃^[11a] during electrolysis and/or formation of dichlorophophorane (Ph₃PCl₂).[11c] Recently, boron esters, [B(OAr)₃], have also been demonstrated to act as suitable LAs to form a Ph₃P=O \rightarrow B(OAr)₃ adduct which facilitates the ratedetermining phosphoryl P=O bond dissociation to form TPP and $[{(ArO)_{3}B}_{2}O]^{2}$ diborate.^[11e] However, its moderate overall efficiency along with side-product formation and the difficulty to recover the boron ester from the diborate limits its suitability for TPP regeneration.^[11e] An improvement in TPP regeneration has lately been achieved under mild electrochemical conditions, in the presence of AlCl₃ as LA and tetramethylethylene diamine as an additive.^[11f] However, the intrinsic dissolution of a sacrificial Al electrode via electro-corrosion and subsequent formation of Al2O3, which has a high energy demand for recycling, limits this approach for sustainable TPP electro-regeneration too.[11a, 11c, 11d, 11f]



Scheme 1. (a) Chemical route of Wittig olefination reations (WOR) followed by chemical recylcing of TPPO to TPP with phosgene (COCl₂) and Al⁰ at 130 ^oC applied by BASF SE for vitamin A production. (b) One-pot electrochemical WOR protocol via cathodic recycling of TPPO without sacrificial electrode and subsequent Wittig yilde regeneration and carbonyl olefination.

On the other hand, and to the best of our knowledge, the direct use of electro-regenerated TPP and base-free electrochemical $Ph_3P=CR_2$ ylide formation and subsequent WOR in the presence

FULL PAPER

of a carbonyl compound in a one-pot protocol is currently unknown.

Herein, we describe a systems approach to a one-pot fully electrochemically driven protocol for direct carbonyl olefination via WOR, combining the required subset of stoichiometric reactions. This includes the recycling of TPPO to TPP in excellent yields omitting any chemical reductant and subsequent in situ electrosynthesis of Wittig ylides in the absence of a base (Scheme 1b).

Starting point is the phosphoryl P=O bond activation of TPPO via *O*-alkylation to form the isolable [Ph₃P(OR)](OTf) phosphoium salts (R = Me (1); Et (2)), using ROTf (OTf = OSO₂CF₃) as sources of R⁺. Structural (XRD), spectroscopic (³¹P NMR, IR) and cyclovoltammometric evidences in support of the P=O bond activation via alkylation is also provided. In the presence of a sub-stoichiometric amounts of Sc(OTf)₃ acting as a very effective redox-innocent Lewis-acidic mediator, the electrochemical conversion of [Ph₃P(OR)]⁺ to TPP could be achieved in 78% (R = Me) and almost quantitative yields for R = Et, respectively, along with ROH alcohol formation. The mechanism and striking role of Sc³⁺ have been rationalized by means of Density Functional Calculations (DFT) (see below).



Figure 1 Activation of the P=O bond in TPPO via methylation with MeOTf to form 1. (a) Downfield shift of 37.9 ppm of the ³¹P NMR signal of TPO (bottom) vs. 1 (top). (b) Anodic shift (870 mv) of the first electron reduction of 1 with respect to TPO (electrochemical condition; 0.15 M TBAPF₆ in CH₃CN with a 0.1 Vs⁻¹ scan rate, glassy carbon (GC) as working, Pt as a counter, Ag as a pseudo reference electrode). (b inset) Molecular structure of the cation in 1 determined by a single-crystal X-ray diffraction analysis; hydrogen atoms of the phenyl rings are ommitted for clarity.

Methyl triflate (MeOTf) was used as a facile source of Me⁺ to activate the P=O bond of TPPO, resulting in almost quantitative isolation of the methoxy-phosphonium triflate, [Ph₃P(OMe)](OTf) 1 (Figs. S1-S4 in Supporting Information). The weakening of the P=O bond via methylation is evident by the large downfield shift in the ³¹P NMR signal of **1** vs. TPPO ($\Delta \delta = 37.9$ ppm) (Fig. 1a), which is further supported by FTIR spectroscopy with a bathochromic shift of the v(PO) stretching vibration mode at 1191 cm⁻¹ for TPPO (Fig. S4). Accordingly, the P-O distance obtained from an X-ray crystal structure alnalysis of 1 (Fig. 1b inset; Tabs. S1, S2) is about 0.08(1) Å longer than that in TPPO.^[12] The activation of the P=O bond in TPPO via formation of 1 further leads to a drastic decrease of the redox potential as evident from the cyclic voltammograms recorded acetonitrile solutions with 0.15 M tetrabutylammonium hexafluorophosphate (TBAPF₆). A pseudo-reversible one-electron-reduction of TPPO was observed at 2.92 V (vs. Fc/Fc⁺)^[10d, 11e, 11f] (Fig. 1b, black curve). The methylation of P=O to P-OMe+ causes an anodic shift of 870 mV

and irreversible reduction of 1 (Fig. 1b, red curve) which, in contrast, has not been previously achieved with TPPO \rightarrow LA (LA: B(OAr)₃ and AlCl₃) adducts, apparently due to weaker association of TPPO and LA.[11e, 11f] However, the estimated free energy change (AG) determined by Density Functional Theory (DFT) calculations for the one-electron reduction of [Ph₃P(OMe)]⁺ (Fig. S5) is about 63.7 kcal mol⁻¹ preferable in comparison to TPPO, while that of the TPPO \rightarrow AlCl₃ adduct is stabilized by only 9-10 kcal mol-1, as reported recently.[11f] Additional four different phosphine oxides (R₃PO) were selected bearing phenyl and/or alkyl substituents R attached to the P center and using the same methodology of phosphoryl P=O bond via alkylation, corresponding methoxy- and/or ethoxy-phosphonium salts [R₃P(OR)](OTf) were synthesized and isolated (see Supporting Information; Figs. S6-S17). In all cases and the shifts of their ³¹P NMR signals and the redox potentials indicate a similar degree of P=O activation as observed for TPPO (Figs. S6-S17, Table S3).

The one-pot electrochemical WOR was perfomed in a customized two-compartment cell equipped with Pt foil as a counter electrode and Ag foil as a working electrode (Pt(+)// (-)Ag, geometric surface area 0.5 x 0.5 cm) separated by glass frit (G4 porosity) (Fig. S18 in Supporting Information) to avoid further oxidation (at the counter electrode) using 1 (0.032 M) at a constant current of 4.5 mA (for 2 h, 32.4 C charge passed) followed by addition of MeOTf (0.048 M) and benzaldehyde (PhCHO, 0.048 M) and subsequent electrolysis of the mixture for additional 40 mins under similar electrochemical condition (entry 1 in Table 1). In the latter case, only a trace amount (<10%, entry 1 in Table 1) of the desired olefin (styrene, PhCH=CH₂) was produced (Fig. S19a), presumably due to the moderate TPP regeneration from 1 (about 39 % yields; Fig. S19b) before subsequent addition of MeOTf and PhCHO. DFT calculation of the free energy change associated with the electro-reduction of 1 suggests a plausible pathway (Scheme S1) and predicts that a sequential two step electron uptake by the methoxyphophonium cation in 1 to the corresponding anion via formation of the neutral mono-radical is energetically favorable. The later steps consist of two parallel pathways, P-O and C-O bond dissociation, with comparable free energy changes (ΔG), -50.3 and -45.4 kcal mol⁻¹, respectively (Scheme S1 in Supporting Information). Most likely, the low selectivity towards TPP formation is presumably due to competitive P-O and C-O bond dissociation. Notably, alkene formation could not be achieved under an identical electrochemical condition only with TPPO which further highlights the significance of P=O bond activation via alkylation (Fig. S20). To increase the TPP regeneration from 1, Sc(OTf)3 was employed as a redox-innocent Lewis acid and MeO⁻ acceptor to accelarate the rate-determining P-O dissociation step. Sc(OTf)3 has already been used in other LA-mediated organic transformations^[13] and for the stabilization of high-valent oxotransition-metal intermediates.^[14] In fact, addition of a substoichiometric amount of Sc(OTf)3 to solutions of 1 and subsequent electrolysis under identical conditions (entry 2 in Table 1, in presence of MeOTf and PhCHO) resulted in a drastic increase in styrene formation to 63% yields (Figs. S21 and S22). The stoichiometry of Sc³⁺ (0.6 molar equivalents) was optimized by means of the highest yield of TPP electro-regeration from 1 (Figs. S23-S26).

FULL PAPER

The efficiency of WOR was further tested with four different potential working electrode materials: Cu, Mg foils, Ni foam (NF, 0.5x0.5 cm, three-dimensional) and glassy carbon rod (GC, 6 mm diameter). Under similar experimental conditions, GC carbon rod (entry 3 in Table 1) delivers a moderate yield (41%) of styrene (Fig. S27 and Fig. S28) while Cu, Mg foils and Ni foam remain ineffective in one-pot WOR due to ineffective TPP formation and unwanted TPPO regeneration by C-OPPh3 bond dissociation (Figs. S29-S31 and Table S4). The highest efficiency on a Ag electrode surface could be ascribed to its higher conductivity which plays an important role in this electrochemical system.[15] Other transitionmetal ions (Fe³⁺, Ni²⁺, Yb³⁺, Zn²⁺) were also probed as potential LAs for electrochemical WOR. In the presence of Yb3+, a conversion of ca. 33% styrene was obtained (entry 4 in Table 1, Fig. S32-S33 in Supporting Information). Unfavorably, the desired electrchemical WOR could not occur in the presence of Fe³⁺, Ni²⁺, Zn²⁺ salts most likely due to the lower reduction potentials of Fe³⁺ (E_{Fe³⁺/Fe}; -0.04 V), Ni²⁺ (E_{Ni2+/Ni}; -0.26 V) and Zn²⁺ (E_{Zn2+/Zn}; -0.76 V)^[16] in comparison with 1 (one-electron-reduction at 2.04 V vs Fc/Fc⁺) (Figs. S34-S35). Thus, the high reduction potential of Yb³⁺ (E_{Yb3+/Yb} -2.37 V) and Sc³⁺ (E_{Sc3+/Sc} -2.03 V)^[16] makes them suitable LAs for electrochemical reduction of 1 to TPP and its disposal for a one-pot WOR. In contrast, the addition of B(OPh)₃ as LA does not result in olefin formation due to relatively low TPP regeneration (ca. 20%) from 1 under the applied experimental conditions (Fig. S36).

The displacement of Ph groups in **1** by alkyl substituents has also a significant influence on the WOR efficiency: using $[Ph_2MeP(OMe)](OTf)$, MeOTf and PhCHO lowers the yields of styrene to 31% (entry 5 in Table 1, Fig. S37-S38), while monoethyl substitution on the P atom ($[Ph_2EtP(OMe)](OTf)$) leds merely to unwanted (P)O-C bond scission and formation of Ph_2EtP=O (entry

Table 1. Screening of reaction conditions; (a) one-pot reaction scheme for electrochemical WOR using $[Ph_2RP(OR^1)]^+$ (R= Ph, Me, Et and R¹ = Me, Et) in presence of sub-stoichiometric amounts of Lewis acid (LA), (b) different $[Ph_2RP(OR^1)]^+$ (c) alkyl electrophiles RX, (d) carbonyl compounds, and (e) olefins produced by electrochemical WOR.



Entry ^a	WE ^b	LA ^c	$[Ph_2RP(OR_1)]^{+d}$	Alkyl electrophile ^e	Carbonyl compound ^f	Olefin	Yield
1	Ag	-	[Ph ₃ P(OMe)] ⁺	MeOTf	PhCHO	PhCH=CH ₂	<10%
2	Ag^{g}	Sc^{3+}	[Ph ₃ P(OMe)] ⁺	MeOTf	PhCHO	PhCH=CH ₂	63%
3	GC^{h}	Sc^{3+}	[Ph ₃ P(OMe)] ⁺	MeOTf	PhCHO	PhCH=CH ₂	41%
4	Ag	Yb^{3+i}	$[Ph_3P(OMe)]^+$	MeOTf	PhCHO	PhCH=CH ₂	33%
5	Ag	Sc^{3+}	[Ph ₂ MeP(OMe)] ⁺	MeOTf	PhCHO	PhCH=CH ₂	31%
6	Ag	Sc^{3+}	[Ph ₂ EtP(OMe)] ^{+j}	MeOTf	PhCHO	PhCH=CH ₂	-
7	Ag	Sc^{3+}	$[Ph_3P(OEt)]^+$	EtOTf	PhCHO	PhCH=CHCH ₃	67%
8	Ag	Sc^{3+}	[Ph ₃ P(OMe)] ⁺	PhCH ₂ Br	PhCHO	PhCH=CHPh	43%
9	Ag	Sc^{3+}	[Ph ₃ P(OMe)] ⁺	MeOTf	CyCHO	CyCH=CH ₂	57%
10	Ag	Sc^{3+}	[Ph ₃ P(OMe)] ⁺	MeOTf	FuCHO	FuCH=CH ₂	46%
11	Ag	Sc ³⁺	$[Ph_3P(OMe)]^+$	MeOTf	Ph ₂ CO	Ph ₂ C=CH ₂	22%

^aReaction conditions: all the experiments were conducted under N₂ atmosphere (glove box), 0.175 M TBAPF₆ as supporting electrolyte, dried CH₃CN prior to use as solvent (total volume 3 mL), electrolysis in separated (by glass frit) two electrode cell setup at a constant current (chronopotentiometry; CP at 4.5 mA) using a Pt foil as counter electrode (0.5 x 0.5 cm working area). ^bworking electrode (WE) (0.5 x 0.5 cm working area). ^c highest yield of TPP and WOR was achieved with 0.02 M (0.6 equiv.) LA. ^delectrolysis (2h) was conducted with 0.032 M [Ph₂RP(OR₁)]⁺ in the presence of 0.6 equiv. LA and formation of TPP was confirmed analyzing the solution by ³¹P(¹H) NMR. ^c0.048 M alkyl halide was added to the working compartment after 2h of electrolysis and stirred for additional 30 minutes to prepare the phosphonium salt in situ. ^f0.048 M aldehyde and/or ketone added further to the working compartment. ^gAg foil 0.1 mm thick connected to with copper wire and copper tape (under an identical condition Cu foil, Mg foil and Ni foam didn't produce alkene), ^hglassy carbon rod (GC; 6 mm diameter). ⁱ0.02 M Yb(OTf)₃; other LA (Fe³⁺, Ni²⁺, Zn²⁺ and B(OPh)₃) remain ineffective for one-pot WOR. ^j[R₃POMe](OTf) (R = n-Bu and n-oct) didn't produce any olefin due to poor TPP regeneration (Figs. S40-41)



FULL PAPER

6 in, Table 1, and Figs. S39-S41). Notably, due to the higher reduction potentials of fully alkyl-substituted phosphine oxides (*n*Bu₃PO, *n*Oct₃PO), electro-chemical and/or chemical reduction remain unfavorable under the here applied conditions.^[8b. 11f] Although DFT calculations performed with [*n*Bu₃P(OMe)]⁺ revealed that the one-electron- reduction of the phosphonium center is energetically favorable, no minima was obtained in the potential energy surface for the two-electron-reduction to *n*Bu₃P (Scheme S2). Conversely, the computed Δ G value for the C-O bond dissociation of [*n*Bu₃P(OMe)]⁺ is energetically favorable and as a consequence, *n*Bu₃PO and *n*Oct₃PO were solely obtained during electroreduction of the respective methoxyphosphonium salts (Scheme S2) and, henceforth, alkyl-substituted methoxy phosphnium salts are unsuitable for electrochemical WOR.

Starting from TPPO, the electrochemical WOR can also be achieved with other alkoxy-phosphonium salts, $[Ph_3P(OR)]^+$ (R = Et) and using various carbonyl compounds (entry 7-11 in Table 1). electrolysis solutions Accordingly. of containing [Ph₃P(OEt)](OTf) (2), EtOTf and PhCHO affords prop-1-enylbenzene in 67% yields (PhCH=CHCH₃, entry 7 in Table 1, inset c; Figs. S42-S44). Very similarly, about 43 % stilbene (entry 8 in Table 1, Figs. S45-S47), 57% vinylcylohexane (CyCH=CH₂, entry 9 in Table 1, Fig. S48), 46% 2-vinalyfuran (FuCH=CH2 entry 10 in Table 1, Fig. S49) and 22% 1,1-diphenylethene (Ph₂C=CH₂, entry 10 in Table 1, Fig. S50) could be prepared. However, electrochemical WOR does not occur with unactivated TPPO in the presence of Sc³⁺ although a week interaction between 'free' TPPO and Sc3+ is suggested by 31P(1H) NMR and also observed for the one-electron redox potential of TPPO in the presence of Sc^{3+} in CV (Fig. S51). This control experiment proves that both alkoxyphosphonium salt and Sc^{3+} are the two key components for successful one-pot electrochemical WOR.

In the earlier reports of electroreduction of TPPO to TPP, the LAs such as B(OAr)₃, AlCl₃ and Me₃SiCl act as sinks to trap O²⁻, producing the very stable $[{(OAr)_3B}_2O]^2$ diborate, ^[11e] Al₂O₃, ^[11f] and (Me₃Si)₂O disiloxane, [11b] respectively. In contrast, the electroreductive P-O bond cleavage of 1 and 2 furnishes the respective alcohols CH₃OH (from 1 in 68 % yields) and C₂H₅OH (from 2 in 75% yields), respectively (see Figs. S52-S54). Core level X-ray photoelectron spectroscopic (XPS) analyses of crude solids isolated from concentrated electrolyzed solutions were performed to determine the valence state of scandium after electrolysis. The binding energies obtained for Sc 3p_{1/2} (407.8 eV) in these solids were identical to that of fresh Sc(OTf)₃ (Fig. S55), proving that Sc remains in the same oxidation state (+3) after the reaction.[17] Although, TPPO can coordinate Sc³⁺ and forms a stable isolable complex,^{[18] 31}P(¹H) NMR and ESI-mass spectra of a mixture of 1 and Sc(OTf)₃ indicated the presence of 'free' 1 in solutions (Figs. S56-S57).

How does the electroreduction of the cation in **1**, [**1** - **OTf**]⁺, occur and what is the role of Sc^{3+} in this process? We propose a plausible mechanistic pathway based on results of DFT calculations as depicted in Figure 2. To explain the reduction of [**1** - **OTf**]⁺ in the presence of Sc^{3+} , geometry optimizations were carried out at the B3LYP^[19a, 19b-d]-D3^[20] level of theory with Stuttgart RSC 1997 valence basis set and effective core potential^[21] for Sc and 6-31G(d,p) basis set^[22] for all other atoms. To account for the solvent effect of acetonitrile, single point calculations of the



Figure 2. Calculated mechanism of electroreduction of 1 to triphenylphosphine (TPP) mediated by Sc^{3+} . The values in eV are shown in parentheses.

FULL PAPER

optimized structures were performed using Polarizable Continuum Model (PCM). The calculations revealed that coordination of Sc³⁺ with [1 - OTf]⁺ is energetically disfavoured, while ligation with acetonitrile takes place rather easy to form complex A. The latter can release one of the coordinating acetonitrile ligands to form the pentacoordinated Sc complex A' but the reaction is slightly endergonic by 4.1 kcal mol⁻¹ (Fig. 2a). Notably, the one-electronreduction product of [1 - OTf]+, that is, the corresponding radical [1 - OTf]; has a highly exergonic coordination affinity towards A' with 57.9 kcal mol⁻¹, affording the Sc-arene π -complex **B** (Fig. 2b); in fact, related scandium-arene complexes have previously been reported.^[23] O- and P-cordination of [1 - OTf] to Sc could lead to the isomer B' and B", respectively (Fig. 2b), but they are less stable than **B**. Upon formation of **B**, the methoxy group on phosphorus can be transferred to the electrophilic CN carbon atom of the ligated acetonitrile via the transition-state TS(B-C) to give the methoxy-acetimidate-substituted Sc complex C; the latter can undergo a one-electron-reduction to form the anionic complex D at $\Delta G = -159.0$ kcal mol⁻¹ (Fig. 2c). **D** releases a 'free' phosphine via **TS(D-E)** forming the complex **E** at $\Delta G = -170.4$ kcal mol⁻¹ in which the methoxy-acetimidate oxygen atom coordinates to the Sc center. Cleavage of the NC-OMe bond of the methyl-acetimidate group via TS(E-F) results in formation of the methoxy-substituted scandium complex F at -187.4 kcal mol⁻¹. Protonation of F can result in formation of methanol (Fig. 2d, as observed experimentally, see also Fig. S52) along with regeneration of A.

After successful regeneration of TPP from 1 and 2, addition of alkyl electrophiles RX (R = Me, Et, benzyl; X = OTf, Br) resulted in the almost quantitative formation of the corresponding phosphonium salts, [TPP-R](X), as evidenced by their downfield ³¹P chemical shifts from $\delta = -5.6$ (TPP) to 21.4 ppm for [TPP-Me]⁺ in the ³¹P(¹H) NMR spectrum (Fig. S58, see Figs. S44a for [TPP-Et]⁺ and S45 for [TPP-CH₂Ph]⁺). Shano et al. proposed that a Wittig vlide can be formed in situ through one-electron-reduction of phosphonium cations.[10b, 24] Up to now, no experimental evidence in support of ylide formation was reported. In fact, electroreduction of in situ regenerated methylphosphonium triflate, [TPP-Me](OTf), from 1 (Fig. S58) and/or independently prepared (Fig. S59) under similar reaction conditions affords the corresponding Ph₃P=CH₂ Wittig ylide as proven by its characteristic ³¹P(¹H) NMR spectrum (Fig. S60); this confirms that the one-pot olefination described herein occurs via in situ Wittig ylide formation (Scheme S4). After complete electrochemical WOR with Ph₃P=CR'₂ (CR'₂ = CH, CHEt, CHPh) ca. 87% TPPO is generated (Fig. S61).

In summary, we reported a novel and facile one-pot electrochemical strategy for Wittig olefination reactions directly recyling TPPO by means of P=O phosphoryl bond activation via alkylation with RX (R = Me, Et; X = OTf) to give [Ph₃P(OR)](OTf), which proved to be a suitable pathway for electro-recycling of TPP with high efficiency (80-98%) in the presence of Sc(OTf)₃ in acetonitrile solutions. DFT calulations shed light into the crucial role of Sc³⁺ and acetonitrile which both act as mediators in the electroreduction of the P-OR bond in [Ph₃P(OR)](OTf) (1 and 2) to form TPP. Interestingly, the formation of alcohol as a value-added side product could be achieved (and explained by the DFT-proposed mechanism) which distincts this approach from previous methods using chemical reductants (e.g., silanes, boranes) and sacrificial electrode material (e.g., Al). Moreover, a separated cell set-up with Ag as a working electrode and Pt as a supporting electrode does not show anodic corrosion and/or electrode dissolution, representing a highly sustainable one-pot approach for WOR. Furthermore, the electroreduction of $[Ph_3P(OR)]^+$ to TPP and subsequent olefination reaction via in situ electrochemical Wittig reagent formation could be realized in a one-pot protocol with extended scope of substrates. The strategy presented herein could pave the way to bulk scale electrochemical WOR synthesis of more functionalized alkenes.

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FULL PAPER

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Fully electrified: For the first time, a electrochemical system for a one-pot Wittig olefination reaction (WOR) is reported, which includes a very efficient recyling of triphenylphosphine from triphenylphosphine oxide waste and subsequent carbonyl olefinations via in situ base-free Wittig ylide formation, avoiding chemical reductants or sacrificial electrodes.



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Page No. – Page No.

A One-Pot Electrochemical Strategy to Wittig Olefinations Avoiding the Use of Chemical Reductant or Sacrifical Electrode