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A Phosphetane Catalyzes Deoxygenative Condensation of α-Keto Esters and Carboxylic Acids via P^{III}/P^{V}=O Redox Cycling

Wei Zhao, Patrick K. Yan, and Alexander T. Radosevich*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

Supporting Information

ABSTRACT: A small-ring phosphacycle is found to catalyze the deoxygenative condensation of α-keto esters and carboxylic acids. The reaction provides a chemoselective catalytic synthesis of α-acyloxy ester products with good functional group compatibility. Based on both stoichiometric and catalytic mechanistic experiments, the reaction is proposed to proceed via catalytic P^{III}/P^{V}=O cycling. The importance of ring strain in the phosphacyclic catalyst is substantiated by an observed temperature-dependent product selectivity effect. The results point to an inherent distinction in design criteria for organophosphorus-based catalysts operating via P^{III}/P^{V}=O redox cycling as opposed to Lewis base (nucleophilic) catalysis.

Catalyzed oxygen-atom-transfer reactions, in both natural[1] and synthetic[2] systems, are a focus of persistent interest. While many of the most significant synthetic O-atom-transfer reactions are oxygenative in nature,[3] opportunity exists to develop synthetically attractive deoxygenative methods with catalysts operating within a suitably reducing redox couple. Along these lines, we recently investigated a deoxygenative condensation of α-keto esters with various protic pronucleophiles mediated by the conversion $R_3P^{III}\rightarrow R_3P^{V}$=O (Figure 1).[4] These transformations are initiated by Kukhtin−Ramirez addition[5] of α-keto ester substrates to a reducing trivalent phosphorus reagent; subsequent proton transfer from a protic pronucleophile and Arbuzov-like displacement of phosphine oxide lead to the observed α-functionalized ester products.[6] We report the finding that a strained small-ring phosphacycle is capable of *catalyzing* the deoxygenative condensation of α-keto esters and carboxylic acids in a manner that involves formal P^{III}/P^{V} oxidation state cycling via in situ reduction of a P^{V}=O linkage by a hydrosilane (Figure 1). These results, which expand the emerging area of phosphine oxide-catalyzed reactions,[7] illustrate the extent to which the design criteria for organophosphorus catalysts operating by P^{III}/P^{V} redox cycling diverge from those of the more well-established organophosphorus-based nucleophilic catalysts. More broadly, the results further suggest opportunities for geometrically constrained main-group compounds as redox catalysts in organic transformations.[8]

The longstanding challenges associated with recycling and turnover of the phosphine oxide byproducts of stoichiometric phosphine-mediated transformations are typically rationalized on enthalpic grounds.[9] Notwithstanding this thermodynamic argument, there exist numerous reagents that promote the conversion P^{V}=O→P^{III} with good chemoselectivity, chief among them being silane-based reductants (R_3Si−H) pioneered by Horner[10] and Mislow.[11] The issue of phosphine oxide reduction, especially in the context of P^{III}/P^{V}=O catalysis, is thus better framed as one of kinetics, with improved rates holding the key to catalytic applications. Several recent reports noted the superiority of cyclic phospholanes in silane-mediated phosphine oxide-catalyzed transformations. In 2009, O'Brien was the first to show P^{III}/P^{V}=O redox catalysis employing a phospholane *P*-oxide in the context of a catalytic Wittig reaction.[12,13] Additional results from O'Brien[14] and Rutjes[15] further established the importance of phosphacycles (e.g., **1** and **2**)[16] in P^{III}/P^{V}=O redox catalysis.[17] However, attempts to employ these catalysts (20 mol% loading) in the deoxygenative condensation of methyl benzoylformate (**6**) and 4-fluorobenzoic acid (**7**) in the presence of phenylsilane as reductant resulted in predominately reduction of **6** to methyl mandelate (**9**) (entries 1 and 2, Table 1).[18] By contrast, we found that use of the highly strained four-membered-ring phosphetane *P*-oxide **3** leads to formation of the deoxygenative condensation product **8** (entry 3), albeit in low yield and as the minor component of the product mixture **8**/**9**. Optimization of catalyst and conditions (entries 4−7) converged on aminophosphetane *P*-oxide **5** as the preferred precatalyst, giving deoxygenative condensation product **8** in 89% isolated yield. This transformation marks a direct catalytic synthesis of α-acyloxy esters from carbonyl and carboxylic compounds that would most commonly be accomplished by two-step carbonyl reduction/acylation strategies. Control experiments (entries 8 and 9) confirm that formation of **8** depends on the presence of a P-based catalyst.

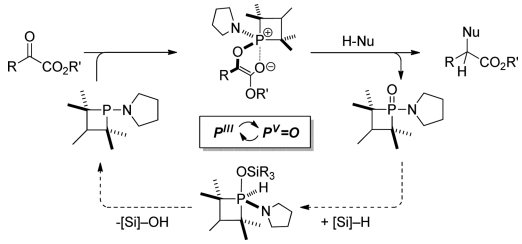

Figure 1. Phosphetane-catalyzed deoxygenative condensation of α-keto esters and protic pronucleophiles via P^{III}/P^{V}=O O-atom-transfer.

Phosphetanes have not featured widely in organophosphorus catalysis,[19] presumably as a function of their perceived instability[20] and the weak nucleophilicity that attends the severe geometric deformation enforced by the small ring (*vide infra*).[21]

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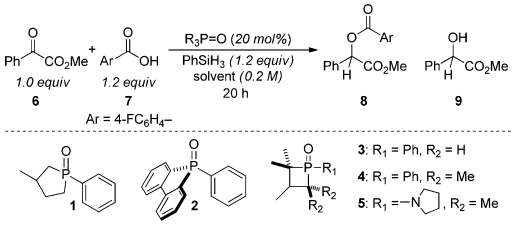
Table 1. Phosphacycles as Catalysts for Deoxygenative Condensation

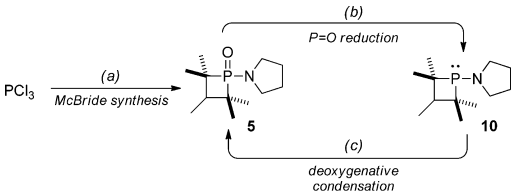


entry	$R_3P{=}O$	solvent	T (°C)	yield[a] (%) 8	9
1[b]	**1**	PhMe	100	0	73
2	**2**	PhMe	100	0	83
3	**3**	PhMe	100	27	47
4[b]	**4**	PhMe	100	41	42
5	**5**	PhMe	100	84	7
6[c]	**5**	PhMe	80	80	
7[c]	**5**	1,2-DCE	80	89	
8	none	1,2-DCE	80	0	0
9	pyrrolidine	1,2-DCE	80	0	0
10[c]	**10**[d]	1,2-DCE	80	73[e]	

[a]Yields of isolated products. Reactions conducted on 0.56 mmol scale. [b]Yields based on recovered starting material. [c]Yield of **9** not determined. [d]See Scheme 1 for structure. [e]See ref 25.

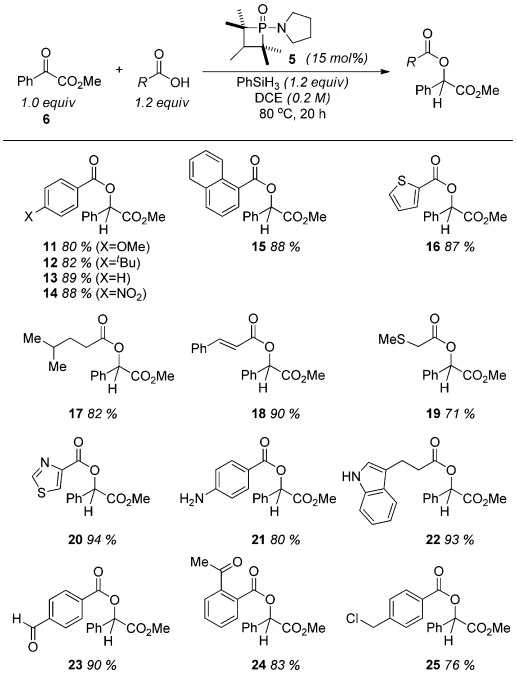
Notwithstanding this fact, phosphetanes of diverse substitution are readily prepared on multigram scale (i.e., via McBride synthesis[22]), and these compounds exhibit the requisite stoichiometric reactivity to underpin the proposed catalytic O-atom-transfer sequence (Scheme 1). Specifically, aminophosphetane *P*-oxide **5** is prepared in 81% yield by reaction of phosphorus trichloride and 2,4,4-trimethyl-2-pentene in the presence of aluminum trichloride, followed by amination of the intermediate phosphinoyl chloride with pyrrolidine.[23] Moreover, the aminophosphetane *P*-oxide **5** is readily reduced by $PhSiH_3$ under mild conditions to the tricoordinate aminophosphetane **10**.[24] Furthermore, tricoordinate **10** promotes the deoxygenative condensation of **6** and **7**, yielding the corresponding α-acyloxy ester **8** with regeneration of aminophosphetane *P*-oxide **5**. Based on these stoichiometric reactivities, we postulate that the deoxygenative condensation observed in Table 1 proceeds by catalytic O-atom-transfer via **5**/**10** cycling. In concert with this proposal, we find that the tricoordinate aminophosphetane **10** also serves as a functional catalyst for the deoxygenative condensation (Table 1, entry 10).[25]

Scheme 1. Preparation and Stoichiometric Reactivity of Aminophosphetanes[a]



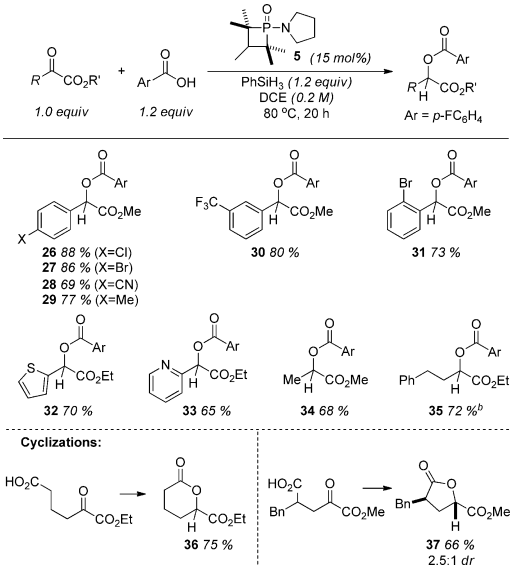
[a]Reagents and conditions: (a) *i.* 2,4,4-trimethyl-2-pentene, $AlCl_3$; *ii.* pyrrolidine, 81% for two steps. (b) $PhSiH_3$, PhMe, rt, 67%. (c) PhC(O)CO_2Me (**6**), *p*-$FC_6CH_4CO_2H$ (**7**), PhMe, 50 °C, 92%.

Table 2. Examples of Deoxygenative Condensation with Varying Carboxylic Acid Components[a]



[a]Yields are for isolated products.

Table 3. Examples of Deoxygenative Condensation with Varying α-Keto Ester Components[a]



[a]Yields are for isolated products. [b]Ar = *p*-^{t}BuC_6H_4–.

The results of our studies into the scope of this catalytic transformation are collected in Tables 2 and 3. With respect to the carboxylic acid component, a suite of benzoic acid derivatives bearing electron-rich (**11**) and electron-deficient substituents (**14**) gave excellent yields of the corresponding α-acyloxy esters. Other carboxylic acids, both saturated (**17**) and unsaturated (**18**), are likewise reductively coupled in excellent yield. The inherently low Lewis acidity of the P-based catalyst results in good compatibility with heteroatom functionality including heteroarenes (**16**, **20**, **22**), sulfides (**19**), and free anilines (**21**). By virtue of the Kukhtin–Ramirez-initiated mechanism, the

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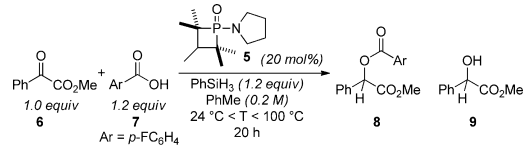
reaction is selective for reductive coupling at the α-keto ester carbonyl; carbonyl functionality elsewhere in the reactants including both ketone (**24**) and even aldehyde (**23**) groups are carried through the transformation without complication. Perhaps most significantly, the phosphetane-catalyzed method shows good chemoselectivity for reductive coupling even in the presence of sensitive electrophilic functionalities that are known substrates for reaction with tricoordinate P compounds. For instance, both electron-deficient nitroarenes (**14**) and benzylic halides (**25**) are unaffected during the event.

The reaction is similarly amenable to diverse α-ketoester substrates (Table 3). Functionalized benzoylformate derivatives were reactive, giving good to excellent yields. Other heteroaromatic α-keto esters (**32**, **33**) were also reactive. Alkyl α-keto esters were found to be suitable substrates for both inter- (**34**, **35**) and intramolecular (**36**, **37**) implementations.

The importance of ring strain in facilitating $P^{III}/P^{V}{=}O$ cycling is illustrated by an observed dependence of product selectivity on temperature. As described above, reaction of **6** and **7** with 20 mol % **5** and 1.2 equiv of phenylsilane at 100 °C in PhMe results predominantly in catalytic deoxygenative condensation product **8** (Table 4, entry 1). Under otherwise identical reaction

Table 4. Dependence of Product Selectivity on Temperature



		yield[a] (%)	
entry	T (°C)	**8**	**9**
1	100	84	7
2	75	73	22
3	50	48	43
4	24	18	74

[a]Yields are for isolated products.

conditions, however, decreasing reaction temperature (entries 2−4) results in an increase in the formation of **9** at the expense of **8**. In each case, the combined yields of **8** and **9** exceed >90%. We independently verified that the reduction product **9** is not an intermediate en route to **8**: (1) the product ratio **8**/**9** for a room temperature reaction (i.e., Table 4, entry 4) remains unchanged upon subsequent heating to 100 °C for 20 h, and (2) resubjection of **9** to the high-temperature conditions depicted in Table 4 (1.0 equiv **9**, 1.2 equiv **7**, 1.2 equiv $PhSiH_3$, 20 mol% **5**, 0.2 M in PhMe, 100 °C, 20 h) does not lead to **8**.[26] Thus, we infer that the observed product ratios are formed under kinetic control. A linear relationship is obtained in the plot of $\ln((\mathbf{8}/\mathbf{9})/T)$ vs $1/T$ (Figure 2), from which an isokinetic temperature (T_{iso} = 48 °C) and differential activation parameters ($\Delta\Delta H^{\ddagger}$ = +10.5(9) kcal/mol, $\Delta\Delta S^{\ddagger}$ = −26(6) cal/mol·K) can be extracted. The interpretation of these values suggests that the process leading to **8** is disfavored relative to **9** on enthalpic terms, but favored at higher temperatures on entropic terms. Moreover, the magnitude of $\Delta\Delta S^{\ddagger}$ is suggestive of differing molecularity in the rate-controlling steps for the formation of **8** and **9**, respectively. In situ spectroscopy at both the high and low temperature extremes show phosphetane *P*-oxide **5** (^{31}P δ 58.8 ppm) to be the only observable P species in solution throughout the course of the catalytic transformation.

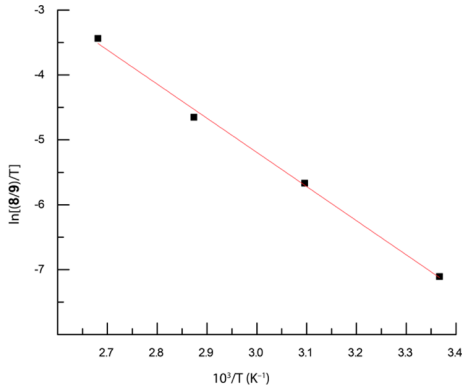


Figure 2. Correlation between product selectivity and temperature over the range 24 °C < T < 100 °C (see Table 4). Linear fit: $\ln[(\mathbf{8}/\mathbf{9})/T] = -5.26T^{-1} + 10.59$, $R^2 = 0.995$.

From these results, we surmise that the consumption of the phosphine oxide by silane represents the selectivity-determining branch point and that the strain imposed at P by the four-membered ring is essential for obtaining the deoxygenative condensation transformation. Previous experimental[27] and theoretical[28] studies implicate an intramolecular hydride shift from Si to P (**38**→**39**, Figure 3) as the rate-controlling step in

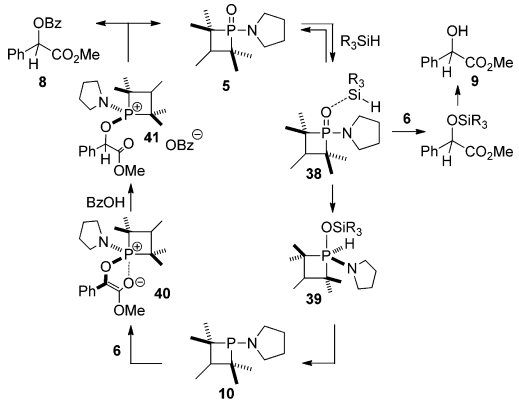


Figure 3. Mechanistic proposal for deoxygenative condensation.

silane-mediated phosphine oxide reduction. The energetic barrier to this transformation is associated with significant bond angle contraction that attends conversion of the pseudotetrahedral phosphine oxide to a trigonal bipyramidal phosphorane. The strain accrued to the phosphetane minimizes the necessary geometric reorganization and thereby increases the rate of $P^{V}{=}O \rightarrow P^{III}$ reduction relative to intermolecular hydrosilylation. This line of reasoning connects with the rationale put forth by Westheimer[29] and Hudson[30] on the effect of ring strain on phosphate and phosphine reactivity, and related arguments underpin the strain-induced Lewis acidity in the main group (P,[31] Si,[32] Ge,[33] Al[34]). Subsequent deoxygenative condensation promoted by tricoordinate **10** via Kukhtin−Ramirez intermediate **40** and **41** then follows to regenerate **5** and close the catalytic cycle.

There is an electronic corollary to the finding that highly strained four-membered phosphacycles enable deoxygenative condensation of α-keto esters and carboxylic acids. The imposition of acute angles at P by the small ring (as in **10**) leads to accrual of *s*-character in the valence lone pair,[35] with a concomitant decrease in nucleophilicity. This phenomenon runs

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counter to the design of typical organophosphorus nucleophilic catalysts,[36] which favor structures with broad interior angles that result in higher energy, *p*-rich frontier lone pairs. Theoretical efforts to substantiate and metrically assess the underlying enthalpic and electronic components of the strained phosphacyclic design are ongoing in our laboratories. Experimental work also continues with the goal of expanding the scope and performance of phosphetane-based P^{III}/P^{V} redox catalysis.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*radosevich@psu.edu

Notes

The authors declare no competing financial interest.

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