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I_2/TBHP Mediated Divergent C(sp^2)-P Cleavage of Allenylphosphine Oxides: Substituent-Controlled Regioselectivity

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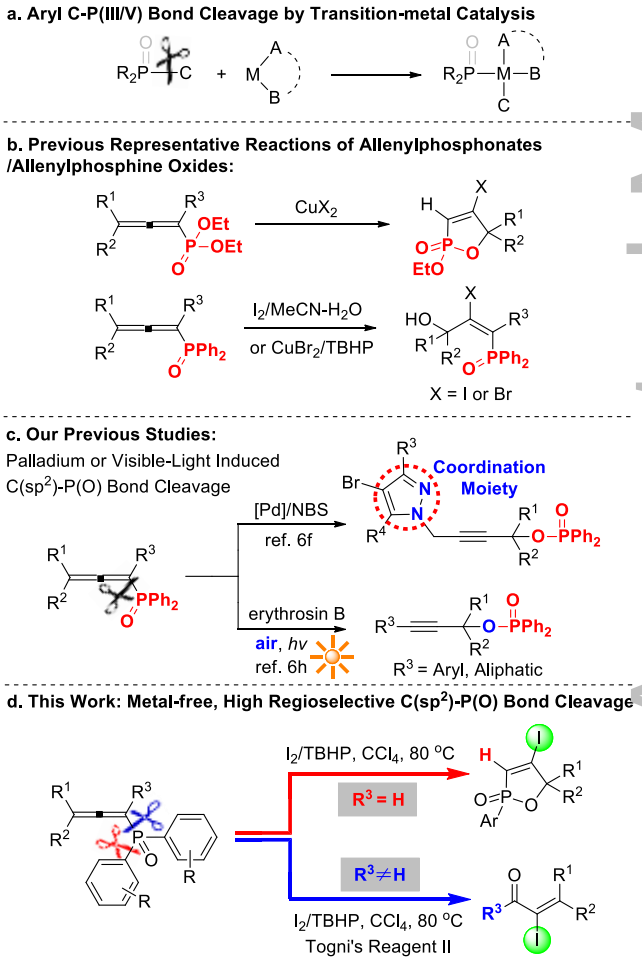
Abstract: A highly regioselective C(sp^2)-P(O) cleavage of allenylphosphine oxides mediated by I_2/TBHP is achieved for the first time. The divergent pathway via cleavage of (Ph)C-P(O) or (allene)C-P(O) modulated by substituents, renders the formation of 4-iodo-2-phenyl-5*H*-1,2-oxaphosphole 2-oxide and *α*-iodoenone derivatives, respectively. A plausible mechanism through radical pathways, along with the cleavage of phenyl and diphenylphosphine oxide moieties, are verified by the trapping experiments and ^{18}O-isotopic labeling studies.

Keywords: Divergent C(sp^2)-P(O) Cleavage; Allenylphosphine Oxides; I_2/TBHP Combination; Metal-Free; Substituent-controlled Regioselectivity

Bond cleavage and reconstruction has always been an attractive topic since it provides a facile pathway for the preparation of value-added products from under-functionalized molecules.[1] Considerable efforts on bond cleavage have long been devoted to that of C-H,[1b,c] C-C,[1d,e] and C-heteroatom,[1f-h] but less is known concerning catalytic C-P bond cleavage,[2] albeit emerging as a hot research topic recently. The privileged strategy in this area mainly concerns the cleavage of C-P(III) bond of arylphosphines, which has been recognized as a possible deactivation pathway in some catalytic processes (**Scheme 1a**).[3] Most of the examples involve the oxidative addition of low-valent Pd-complex to the C-P bond, and only a handful of other transition metal complexes, such as nickel[3c,3i] and rhodium,[3h] has been reported. For an elegant work, in 2017, Morandi reported a palladium-catalyzed carbon-phosphorus bond metathesis by reversible arylation,[3j] which intrinsically involved in sequential cleaving aryl C-P bond.



Scheme 1. (a) Aryl C-P Bond Cleavage by Transition-metal Catalysis; (b) Previous Representative Reactions; (c) Our Previous Studies; (d) This Work.

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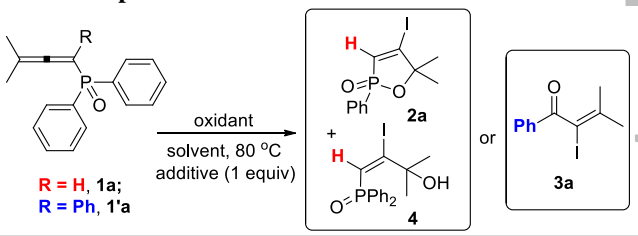
As an important subclass of organophosphorus compounds, phosphine oxides/phosphonates are well-known in regulating biological and medicinal functions.[4] Among which, allenylphosphine oxides and allenylphosphonates have been extensively explored in synthesizing potential bioactive phosphorus-containing heterocycles/homocycles or halogen addition reactions (**Scheme 1b**).[5] However, for overall of the organophosphorus chemistry, the C(sp^2)-P(O) bond cleavage reactions are rather limited and rarely observed due to their high stability.[5g,6] Among these reports, our group recently developed a novel palladium-catalyzed alkenyl C-P(O) cleavage of tetra-substituted allenes, assisted by NBS and the directing of a pyrazole moiety (**Scheme 1c**).[6f] Later on, a novel strategy on cleavage of alkenyl C-P(O) bond by photocatalysis was revealed by us, which featured metal-free and coordination-group-free (**Scheme 1c**).[6h] Although achievements have been made, the reported strategies still suffer from several drawbacks such as air-sensitive transition metal complexes, low yields, limited substrate scope or preinstalled directing/activating groups. The selective cleavage of C(sp^2)-P(O) bond which is still considered to be extremely resistant to chemical cleavage activation, remains challenging. Exploitation of novel and generally applicable C(sp^2)-P(O) bond activation procedures are still highly desirable, especially if tunable chemoselectivity could be achieved and allow for further functionalization to obtain diverse target compounds.

The combination of iodine source/TBHP (*t*-butyl hydroperoxide) as a classic and well-known metal-free system has been proved particularly useful in C-H, C-C and C-N bond formation and activation, as well as selective bond cleavage.[7] The results provide much hope that I_2/TBHP may be extended to cleave the C-P bond. More importantly, when P(O) is tethered with different unsaturated hydrocarbons, the controllable selective cleavage has never been explored as far as we know. Inspired by the afore-mentioned studies and our continued interest in carbon-heteroatom bond cleavage and functionalization,[6f,6h,7e,8] herein, we reveal an unprecedented C(sp^2)-P(O) cleavage strategy featuring high regioselectivity and metal-free manner (**Scheme 1d**).

At the outset of our studies, it was found that in the presence of I_2, TBHP and toluene as solvent, (Ph)C-P(O) bond cleavage did occur for allenylphosphine oxide (**1a**), furnishing 4-iodo-5,5-dimethyl-2-phenyl-5H-1,2-oxaphosphole 2-oxide (**2a**) in 10% yield *via* an intermolecular cyclization (Table 1, entry 1). ***Notice that this type of cyclization is mechanistically distinct from previous reported cyclization of 1,2-alkadienylphosphonate derivatives,***[5d,9] ***since phenyl group is far difficult to leave than that of alkoxyl groups.*** Meanwhile, a large amount of iodo-hydroxylation **4** were produced from iodine and water, which could be a crucial intermediate and has been extensively studied by Ma's group.[5f] To our delight, the ratio between **2a** and **4** exhibited obvious sensitivity to the solvents used. CCl_4 prominently diminished the generation of **4** and gave a highest yield of **2a** in 81% at the same time (entry 5, see details in Supporting Information). Moreover, when other iodine sources such as NIS and KI were tested instead of I_2, only 41% or 20% of **2a** was obtained respectively (entries 6, 7). Interestingly, once the substrate was changed to a tetra-substituted one (**1'a**), (allene)C-P(O) bond cleavage turned to be the major pathway, leading to the formation of α-iodoenone (**3a**) in 41% yield (entry 11).[10] Condition optimizations showed that other solvents entirely inhibited the cleavage, and Togni's reagent II as an additive efficiently enhanced the isolated yield up to 77% (entry 12, also in S.I.). In addition, control experiments were conducted for two pathways. Unsurprisingly, in the absence of I_2 or TBHP, ineffective processes were observed with either lower yields or poor selectivity (entries 8-9, 16-17). Anhydrous system containing TBHP in decane and commercial CCl_4 were further applied, albeit led to no difference in the yields (entries 10, 18). The above results collectively indicated that the combination of I_2 and TBHP were essential to the C(sp^2)-P(O) bond cleavage and suppression of the by-product, and the cleavage pathways strongly depended on the substitutions of substrates.

Table 1. Optimization of the Reaction Conditions[a]



entry	solvent/[I] source/ oxidant/additive	R	Yield of **2a**,**4**/**3a** (%)
1	toluene/I_2/TBHP	H (**1a**)	10, 87/-
2	DMF/I_2/TBHP	H (**1a**)	trace, 95/-
3	CH_3CN/I_2/TBHP	H (**1a**)	trace, 96/-
4	DCE/I_2/TBHP	H (**1a**)	75, <10/-
5	**CCl_4/I_2/TBHP**	**H (1a)**	**81, trace/-**
6	CCl_4/NIS/TBHP	H (**1a**)	41, 30/-
7	CCl_4/KI/TBHP	H (**1a**)	20, 53/-
8	CCl_4/-/TBHP	H (**1a**)	N.R./-
9	CCl_4/I_2/-	H (**1a**)	0, 97/-
10[b]	CCl_4/I_2/TBHP	H (**1a**)	81, trace/-
11	CCl_4/I_2/TBHP	Ph (**1'a**)	-/41
12	**CCl_4/I_2/TBHP/ Togni's Reagent II**	**Ph (1'a)**	**-/77**
13	CCl_4/I_2/TBHP/KIO_3	Ph (**1'a**)	-/52
14	CCl_4/I_2/TBHP/$NaIO_4$	Ph (**1'a**)	-/65
15[c]	CCl_4/I_2/TBHP/ Togni's Reagent II	Ph (**1'a**)	-/57
16	CCl_4/-/TBHP/	Ph (**1'a**)	-/N.R.

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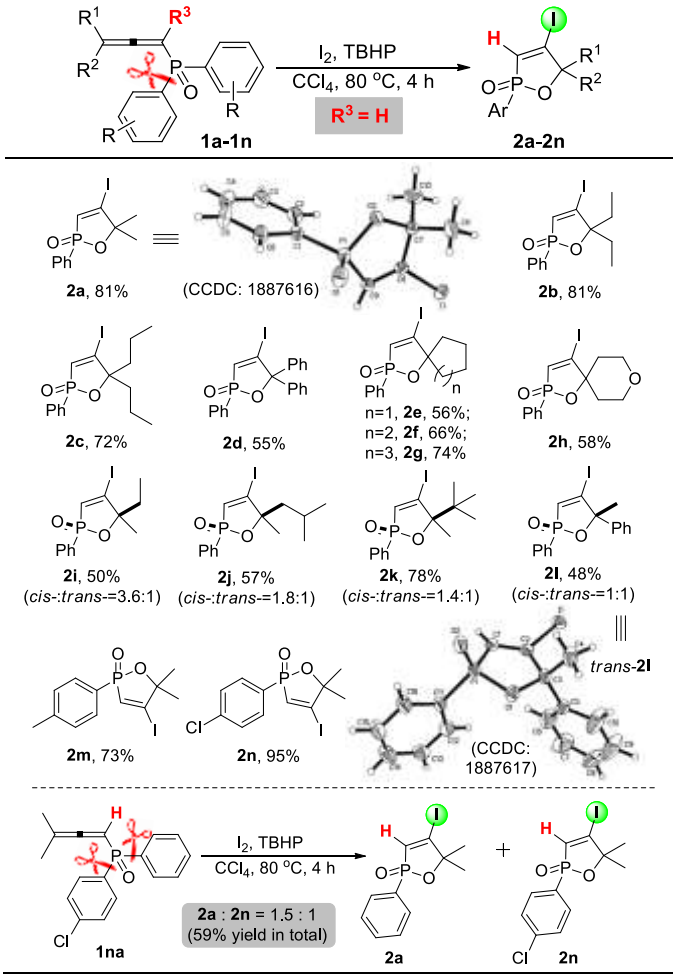
	Togni's Reagent II		
17	CCl_4/I_2/- /Togni's Reagent II	Ph (**1'a**)	-/trace
18[b]	CCl_4/I_2/TBHP/ Togni's Reagent II	Ph (**1'a**)	-/77

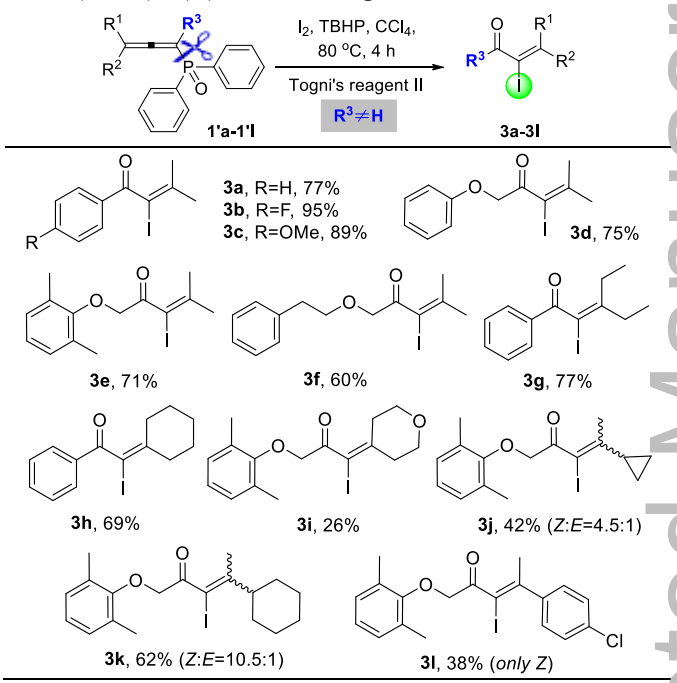
[a] Reaction conditions: phosphinyl allene (**1a** or **1'a**, 0.2 mmol), I_2 (1.0 equiv), TBHP (2.0 equiv), commercial solvent (2 mL), 80 °C, 4 h; Isolated yield, N. R. = No Reaction;
[b] TBHP in *n*-decane and commercial CCl_4 were used;
[c] 0.5 equiv Togni's Reagent II.

Scheme 2. Substrates Scope on Allenylphosphine Oxides for (Ph)C-P(O) Bond Cleavage



Encouraged by the preliminary results, we next evaluated the substrate scope of various allenylphosphine oxides for the reaction of (Ph)C-P(O) bond cleavage toward 1,2-oxaphosphole 2-oxides. As shown in **Scheme 2**, allenylphosphine oxides with symmetrical alkyl, cyclic, heterocyclic or aromatic terminal substitutions were well-tolerated in the system, affording the corresponding cyclic phosphine oxides **2a-h** in moderate to good yields. The X-ray analysis of **2a** (CCDC 1887616)[11] confirmed the structure of 2-phenyl-1,2-oxaphosphole 2-oxides with an iodine substitution. When substrates bearing endmost unsymmetrical substitutions were used, desired products were smoothly delivered as well in yields ranging from 48%-78%, along with diastereo-diversity produced. Substrates of **1i-k** bearing two alkyl substitutions showed a certain diastereo-selectivity preference in ratios of 3.6:1-1.4:1 for *trans*-products (**2i-k**), while only equal amounts of isomers could be isolated for **2l**. ORTEP representation of the **2l** isomer was further obtained (CCDC 1887617)[11] which clearly demonstrated the spatial alignment of methyl and phenyl to the oxygen atom. Arylphosphine oxides (**1m**, **1n**) besides phenyl group could also be ideal substrates for (Ar)C-P(O) cleavage. For allenylphosphine oxide bearing two different aryl groups (**1na**), we found that both of the C-P bonds could be cleaved, but a slight preference on cleaving the electron-deficient phenyl ring was observed, which might be ascribed to the leaving priority of chlorophenolate than phenolate.

Scheme 3. Substrates Scope on Allenylphosphine Oxides for C(allene)-P(O) Bond Cleavage



After a broad scope of tri-substituted allenyl-phosphine oxides was examined, tetra-substituted substrates were further investigated under optimal conditions to obtain diverse *α*-iodo-enones through (allene)C-P(O) bond cleavage (**Scheme 3**). With dimethyl terminated allenylphosphine oxides as substrates, R^3 of aryl, aryl ether and benzyl ether all proceeded smoothly to furnish the desired products (**3a-3f**) in good to excellent yields. It was noted that both an electron-deficient group (*p*-F) and electron-rich group (*p*-MeO) on the phenyl ring were compatible to achieve the reaction (**3b** and **3c**), but electron-deficient group might lead to higher yield. ***Quite interestingly, the allenes bearing etheric substitution (1'd-1'f, 1'i-1'l) were rather labile to undergo C-O(Ar) cleavage upon radical, transition-metal-catalysis and photoredox protocols,[8a-d] however, the C-P(O) bond cleavage turned to be highly regioselective under the current strategy.***

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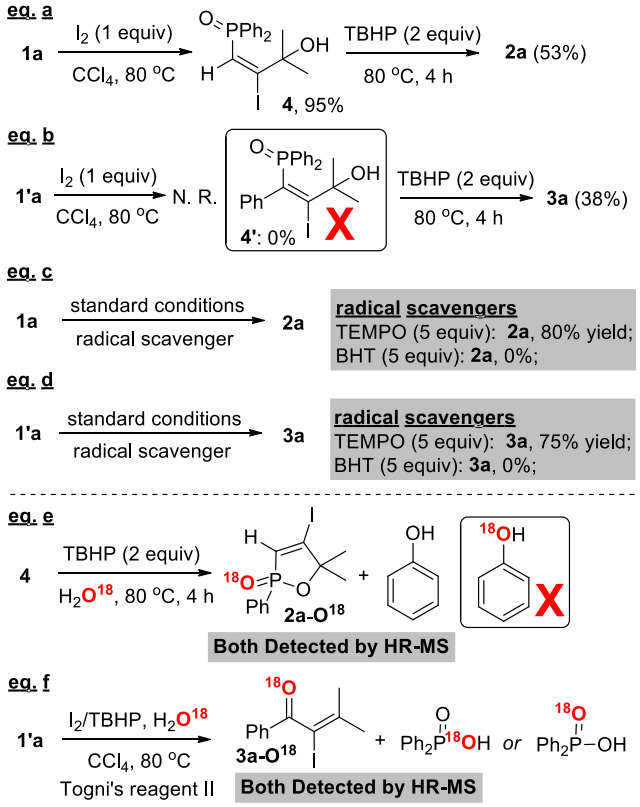
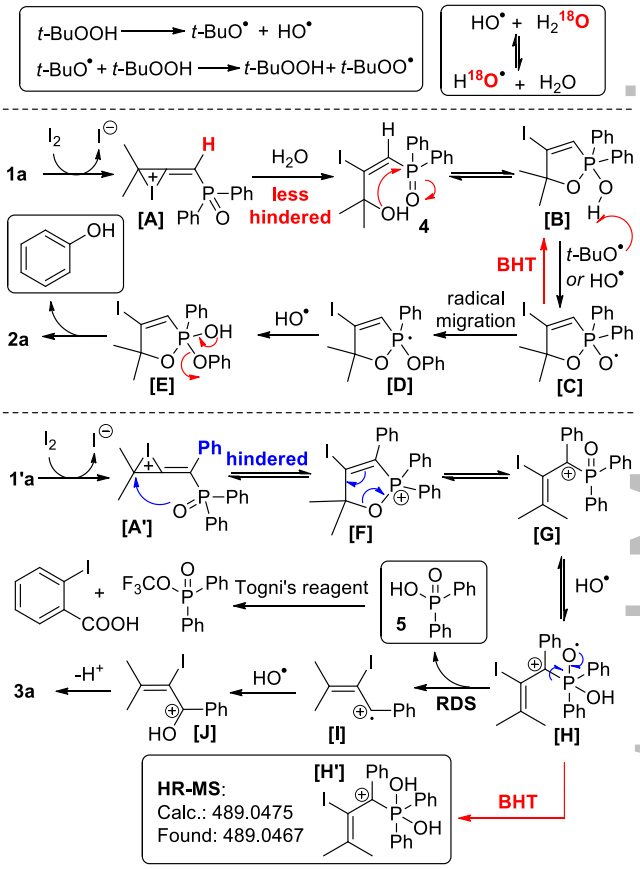
When changing the terminal dimethyl into diethyl, cyclohexyl and heterocyclic groups, effective (allene)C-P(O) bond cleavage were still observed rendering the corresponding *α*,*β*-unsaturated ketones with yields of 77%, 69%, and 26% respectively (**3g-i**), which further demonstrated the high compatibility of the system. Notably, variation of R^1 and R^2 groups would produce stereodiversity, depending on the substitutions of double bonds. Substrates **1'j-l** bearing four different substitutions afforded the corresponding *α*-iodo-enones (**3j-l**) with apparent *Z*-preference, especially for **3l**. It was worthy to mention that the three-membered ring of **3j** survived in the process, without observation of ring-opening product.



Scheme 4. Mechanism Studies

To in-depth perceive the reaction mechanism, several control experiments were conducted as described in **Scheme 4**. In terms of (Ph)C-P(O) cleavage, the pre-prepared iodohydroxylation intermediate (**4**), while being treated with 2 equivalents of TBHP, could be converted into the final product **2a** in 53% yield (eq. a). However, the tetra-substituted allene (**1'a**) was inert to iodine in CCl_4, without formation of iodohydroxylation product which was in line with the previous report.[5f] Further treatment of the crude mixture with 2 equivalents of TBHP gave **3a** in 38% yield (eq. b). Although both reactions could not be inhibited by TEMPO, the addition of BHT efficiently ceased the C-P cleavage reactions (eqs. c and d), indicating possible radical pathways. Moreover, to study where the oxygen comes from and the cleaved species leave, ^{18}O-labeling experiments were performed using **4** and **1'a** as substrates (see more details in S.I.). When using $H_2{}^{18}O$ and TBHP in *n*-decane to do the labeling experiments, the isotopic oxygen was incorporated into final products (**2a-O**^{18}, **3a-O**^{18}) monitored by HR-MS (eqs. e and f). Interestingly, the cleaved moieties were trapped as phenol and ^{18}O-labeled diphenylphosphinic acid, respectively. This result revealed that the oxygen of phenol originates from **4**, and the oxygen of rest products comes from either $H_2{}^{18}O$ or TBHP since hydroxyl radical produced from TBHP can readily exchange with $H_2{}^{18}O$. The control experiments and isotopic distribution information collectively pointed to disparate pathways.



Scheme 5. Proposed Mechanism

On the basis of above facts and related reports,[5f,12] a tentative mechanism for the selective C(sp^2)-P(O) cleavage is proposed in **Scheme 5**. Initially, the iodonium intermediates **[A]**/**[A']** are produced by the reaction of distal double bond with I^+. On one hand, when R^3 equals to H, water molecule attacks **[A]** to form iodohydroxylation intermediate **4**. A reversible nucleophilic cyclization affords **[B]**, which undergoes hydrogen abstraction by *t*-BuO· or HO·, in-situ generated from the decomposition of TBHP, to produce a radical species **[C]**. This step can be inhibited by BHT through hydrogen abstraction and go back to the intermediate **4** (see details in S.I.). Otherwise, phenyl radical migration[12b] from phosphorus atom to oxygen leads to **[D]**, and

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subsequent radical coupling with HO· forms the final product **2a**, accompanied by releasing phenol. On the other hand, when R^3 equals to bulky group instead of hydrogen, the neighboring group participation overwhelms the previous pathway, and enables **[A']** to deliver a five-membered intermediate **[F]**. Reversible ring-opening gives a cation **[G]**, and an intermediate **[H]** is subsequently obtained from the reversible radical addition of HO· to **[G]**. The existence of intermediate **[H]** was verified by BHT inhibition experiment, with a key cation **[H']** detected by HR-MS (see details in S.I., page S10-11). *β*-Scission of **[H]** releases diphenylphosphinic acid and a radical cation **[I]**, which captures hydroxyl radical to finalize **3a** after releasing a proton. Togni's reagent II is supposed to consume diphenylphosphinic acid thus accelerates the rate-determine step (RDS) from **[H]** to **[I].**

In summary, we have revealed a novel strategy on high regioselective cleavage of C(sp^2)-P(O) bonds with the combination of I_2/TBHP. The substituent-dependent cleavage of multi-substituted allenyl-phosphine oxides resulted in divergent formation of 4-iodo-2-phenyl-5*H*-1,2-oxaphosphole 2-oxide and α-iodo-enone derivatives in good to excellent yields, respectively. This strategy features operational simplicity, metal-free manner, and expands the portfolio of organophosphorus chemistry in selective bond cleavage.

Experimental Section

General Procedures for the C(sp^2)-P(O) Bond Cleavage of Allenylphosphine Oxides.

(Ph)C-P(O) Cleavage: To a 5 mL flask was added allenylphosphine oxides (R^3=H) (0.2 mmol), I_2 (50.8 mg, 0.2 mmol), TBHP (51.5 mg, 0.4 mmol) and 2 mL CCl_4. The reaction mixture was then heated to reflux for 4 hrs until the complete consumption of starting materials monitored by TLC. After all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography (eluent: 1:1 (v/v) of ethyl acetate/petroleum ether) to afford product as a white solids.

(allene)C-P(O) Cleavage: To a 5 mL flask was added allenylphosphine oxides (R^3≠H) (0.2 mmol), I_2 (50.8 mg, 0.2 mmol), TBHP (51.5 mg, 0.4 mmol), Togni's Reagent II (63.2 mg, 0.2 mmol) and 2 mL CCl_4. The reaction mixture was then heated to reflux for 4 hrs until the complete consumption of starting materials monitored by TLC. After all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography (eluent: 1:100 (v/v) of ethyl acetate/petroleum ether) to afford product as a viscous pale purple oil.

Acknowledgements

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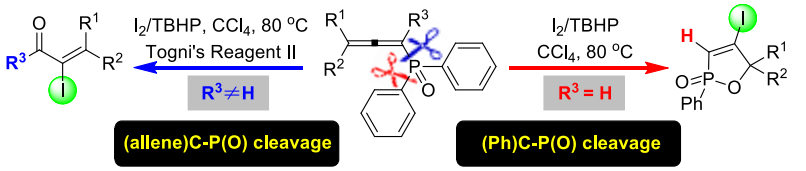
COMMUNICATION

I_2/TBHP Mediated Divergent C(sp^2)-P Cleavage of Allenylphosphine Oxides: Substituent-Controlled Regioselectivity



- ***Unprecedented Divergent Cleavage of C(sp^2)-P bond***
- ***Metal-free, Substituent-controlled Regioselectivity***
- ***27 examples in total, yield up to 95%***

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Teng Liu, Jie Zhu, Xue Sun, Liang Cheng, and Lei Wu*

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