

Preview

Open Access



Recent advances in radical phosphorylation

Yuan Niu, Shang-Dong Yang*

State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, Gansu, China.

*Correspondence to: Dr. Shang-Dong Yang, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, No. 222 South Tianshui Road, Lanzhou 730000, Gansu, China. E-mail: yangshd@lzu.edu.cn

How to cite this article: Niu Y, Yang SD. Recent advances in radical phosphorylation. *Chem Synth* 2021;1:12. <https://dx.doi.org/10.20517/cs.2021.14>

Received: 15 Oct 2021 **Accepted:** 28 Oct 2021 **Published:** 9 Nov 2021

Academic Editor: Bao-Lian Su **Copy Editor:** Xi-Jun Chen **Production Editor:** Xi-Jun Chen

As an important class of chemical molecules, organophosphorus compounds play an irreplaceable role in human industry and life^[1-3]. Therefore, the construction of phosphorus-containing compounds has attracted significant attention from organic chemists. In recent years, there have been advances made beyond the traditional C-P bond formation strategy such as the Arbuzov reaction, Hirao reaction, Friedel-Crafts-type reaction of PCl_3 with aromatic compounds, and the reactions of organometallic reagents with electrophilic phosphorus species^[4,5]; the construction of X-P (X=C, N, O, or S) bonds with P-centered radicals has created a new avenue for the construction of organophosphorus compounds [Figure 1]^[6-11]. In the latest issue of *Chemical Synthesis*, Liu *et al.*^[12] reviewed the recent advances in transition metal-catalyzed, photocatalyzed, and electrocatalyzed C-P, N-P, S-P, and O-P bond formation based on P-centered radicals in the past five years, and some earlier pioneering works were also discussed.

In the review, Liu *et al.*^[12] first briefly introduced the geometries of P-centered radicals and general methods for generating P-centered radicals and also exhibited some common structures of photocatalysts used in phosphorylation reactions. Subsequently, the authors described in detail the radical functionalization of alkenes based on P-centered radicals with different strategies including visible light photoredox-catalyzed reactions and transition metal-catalyzed reactions. In the visible light photoredox-catalyzed reactions, in addition to traditional metal photosensitizers, some organic dyes like Eosin Y can also promote this kind of reaction as well. This summary could play a certain guiding role in the subsequent reaction design. Additionally, a series of P-centered radicals-based difunctionalization of alkenes were also discussed in the section.



© The Author(s) 2021. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.



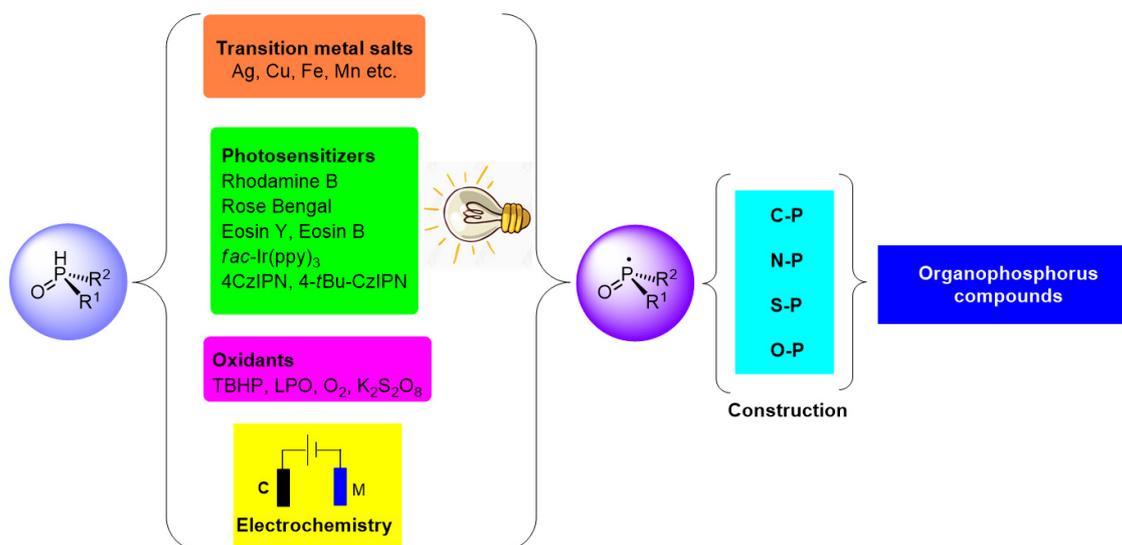


Figure 1. Strategies for constructing organophosphorus compounds by generating P-centered radicals.

Liu *et al.*^[12] then summarized the radical phosphorylation of alkynes. In addition, the authors also focused on the discussion of difunctionalized phosphorylation of alkynes. Furthermore, π -conjugated phosphine molecules have become vitally important in the blooming area of organic light-emitting diodes and photovoltaic cells. The radical cascade cyclization phosphorylation of alkynes has also been well developed and was included in this review. Moreover, arylphenylisonitriles, which contain a $C\equiv N$ π -bond and have good radical acceptor properties, were also compatible with radical phosphorylation though visible light-induced cascade reaction.

Liu *et al.*^[12] continued to introduce the cross-coupling phosphorylation reactions of (pseudo) halides via transition-metal and photoredox dual catalysis. Moreover, decarboxylative or denitro phosphorylation and dehydrogenative C-H phosphorylations were also discussed in the review.

In the final section of their review, Liu *et al.*^[12] summarized several other types of radical phosphorylation such as $C(sp^3)$ -P bond formation via C-C and P-H bond cleavages and Atherton-Todd-type reaction. Notably, electrochemical oxidative phosphorylation with hydrogen evolution was also discussed.

In summary, Liu *et al.*^[12] provided readers with an overview of transition metal-mediated and photoredox-catalyzed radical phosphorylation reactions. At the same time, the review also introduced the method of electrochemical phosphorylation to synthesize organophosphorus compounds. The authors summarized the latest advances on phosphorylation reaction over the past five years. Furthermore, on the basis of this review, the authors put forward their own views on phosphorylation and prospects for the future. This information provided valuable insights and guidelines for the design of such reactions.

DECLARATIONS

Authors' contributions

Prepared the manuscript: Niu Y, Yang SD

Availability of data and materials

Not applicable.

Financial support and sponsorship

We are grateful to the NSFC (No. 21532001) for financial support.

Conflicts of interest

Both authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2021.

REFERENCES

1. Tang W, Zhang X. New chiral phosphorus ligands for enantioselective hydrogenation. *Chem Rev* 2003;103:3029-70. [DOI](#) [PubMed](#)
2. Demmer CS, Krogsgaard-Larsen N, Bunch L. Review on modern advances of chemical methods for the introduction of a phosphonic acid group. *Chem Rev* 2011;111:7981-8006. [DOI](#) [PubMed](#)
3. Duffy MP, Delaunay W, Bouit PA, Hissler M. π -conjugated phospholes and their incorporation into devices: components with a great deal of potential. *Chem Soc Rev* 2016;45:5296-310. [DOI](#) [PubMed](#)
4. der Jeught S, Stevens CV. Direct phosphorylation of aromatic azaheterocycles. *Chem Rev* 2009;109:2672-702. [DOI](#) [PubMed](#)
5. Shao C, Xu W, Li L, Zhang X. Recent Advances of transition metal-catalyzed P-C coupling reactions. *Chin J Org Chem* 2017;37:335. [DOI](#)
6. Gao Y, Tang G, Zhao Y. Recent progress toward organophosphorus compounds based on phosphorus-centered radical difunctionalizations. *Phosphorus Sulfur Silicon Relat Elem* 2017;192:589-96. [DOI](#)
7. Lan X, Wang N, Xing Y. Recent advances in radical difunctionalization of simple alkenes: recent advances in radical difunctionalization of simple alkenes. *Eur J Org Chem* 2017;2017:5821-51. [DOI](#)
8. Gao Y, Tang G, Zhao Y. Recent advances of phosphorus-centered radical promoted difunctionalization of unsaturated carbon-carbon bonds. *Chin J Org Chem* 2018;38:62. [DOI](#)
9. Cai B, Xuan J, Xiao W. Visible light-mediated C P bond formation reactions. *Science Bulletin* 2019;64:337-50. [DOI](#)
10. Chen L, Liu X, Zou Y. Recent advances in the construction of phosphorus-substituted heterocycles, 2009-2019. *Adv Synth Catal* 2020;362:1724-818. [DOI](#)
11. Ung SP, Mechrouk VA, Li C. Shining light on the light-bearing element: a brief review of photomediated C-H phosphorylation reactions. *Synthesis* 2021;53:1003-22. [DOI](#)
12. Liu J, Xiao H, Fu Q, Yu D. Advances in radical phosphorylation from 2016 to 2021. *Chem Synth* 2021;1:9. [DOI](#)