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A Modular Three-Component Approach for Site-selective Tandem Arene Thiophosphorylation

Ziyu Gan, Shuyang Liu, Jiajin Chen, Ziyang Chen, Yongqiang Zhang, Lifang Wang, Han Wang, Yihao Li, and Yunhe Jin*

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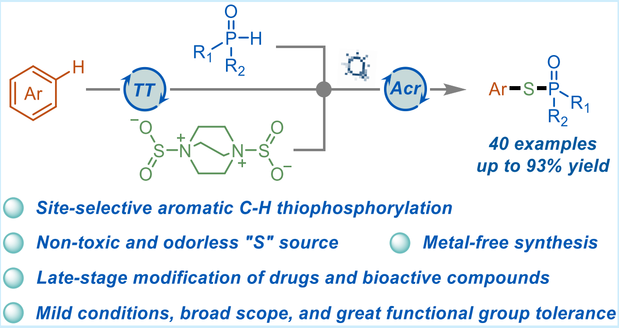
ABSTRACT: Thiophosphates serve as pivotal reagents within the realms of both organic and inorganic synthesis, with their most notable applications observed in agricultural chemistry. This manuscript delineates a modular three-component synthetic strategy for site-selective arene C−H thiophosphorylation with thianthrenium salt, 1,4-diazabicyclo[2.2.2]octane-sulfur dioxide (DABSO), and diarylphosphine oxides as substrates. This approach facilitates the metal-free and green synthesis of a diverse spectrum of *S*-aryl phosphorothioates through C−H functionalization and late-stage modification showcasing practicality and broad applicability.



Sulfur-bearing organophosphorus compounds have garnered significant interest because of their multifaceted roles as versatile reagents in organic synthesis and their critical applications in medicinal chemistry[1] and agrochemistry.[2] These structural motifs have been extensively utilized as convenient precursors for the generation of a wide array of organophosphorus derivatives in synthetic chemistry[3] and protective groups in oligonucleotide synthesis. Notably, many entities within this category manifest exceptional biological activities (Scheme 1a). Omethoate functions as a systemic organophosphate insecticide and acaricide by infiltrating plants to effectively control a broad spectrum of pests by disrupting their nervous systems.[4] Inezin is found to exhibit similar pesticide properties to the organophosphate family by targeting agricultural pests through neurotoxic mechanisms.[5] Iprobenfos, distinct as a phosphorothioate compound, serves as an insecticidal agent by offering protection against soilborne insects through direct contact and ingestion and thereby safeguarding crops from below-ground threats.[6] Consequently, the pursuit of gentle and efficacious methodologies for phosphorothioate assembly is highly desirable, albeit fraught with challenges.

Traditional synthetic strategies for thiophosphate fabrication predominantly depend on nucleophilic substitution reactions (Scheme 1-b1).[7] These conventional techniques frequently require the preactivation of organophosphorus substrates *via* the introduction of various leaving groups, a step often accompanied by the instability of reaction intermediates and the necessity for stoichiometric activating agents.[8] To address these limitations of moisture-sensitive P-reactant preparation and harsh reaction conditions, an innovative synthetic protocol employing $R_2P(O)$-H directly as a substrate was developed by Han with metal catalysts, bases, and oxidants to achieve the desired transformation (Scheme 1-b2).[9a] In the same year, Li and Zhang et al. reported a similar cross-coupling of thiols with $R_2P(O)-H$ under irradiation of visible light and air atmosphere.[9b] Nonetheless, toxic thiophenols and thiols were still ineluctable. In order to surmount this obstacle, Hong et al. achieved the metal-free synthesis of phosphates utilizing benzenesulfonic acid and diarylphosphine oxides in the next year (Scheme 1-b3).[10] Subsequently, Wang et al. reported the copper-catalyzed synthesis of phosphorothioates with diarylphosphine oxides and benzenesulfonyl chloride as substrates (Scheme 1-b4).[11] Despite advancements, issues like high reaction temperatures and the use of toxic, malodorous, and unattainable sulfur-containing precursors remain, thereby rendering 1,4-diazabicyclo[2.2.2]octane-sulfur dioxide (DABSO) a stable, odorless, operationally advantageous, and environmentally friendly S source for modular synthesis.[12] Impressively in 2017, Wu et al. developed a phosphorothioate synthesis strategy with DABSO as the S source in which the diaryliodonium salts that limit the substrate scope and noble metal photocatalyst were still essential.[12c]

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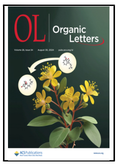

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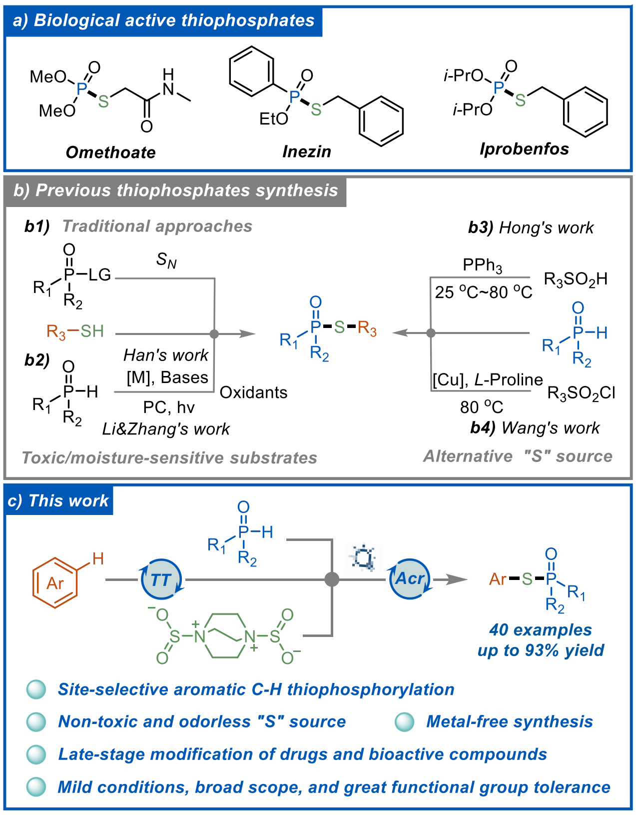
Scheme 1. Approaches for Construction of Thiophosphates



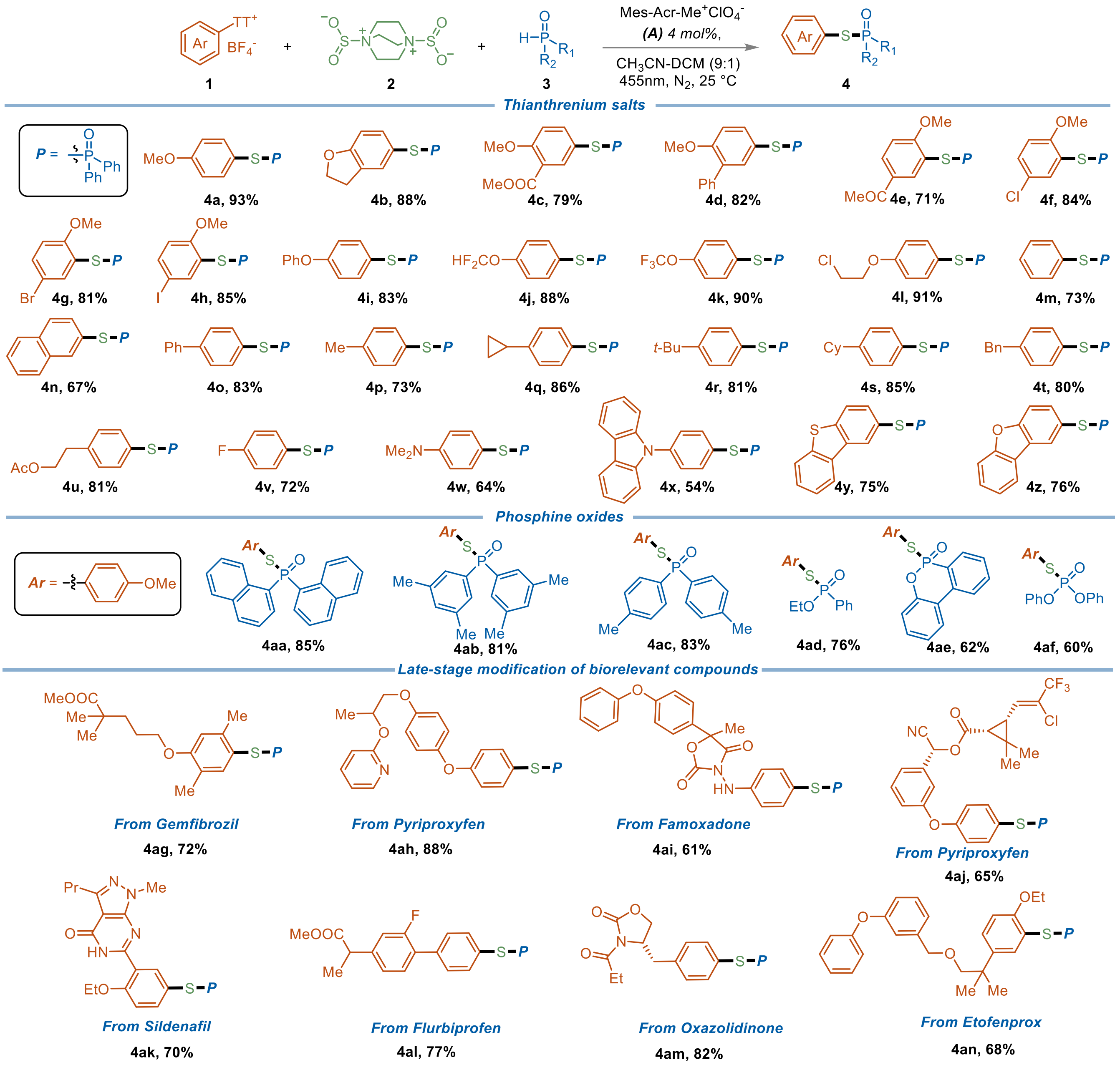
The direct functionalization of aromatic $C(sp^2)$−H bonds represents a prized tactic in the metamorphosis of intricately structured or heavily functionalized molecules, employing inert C−H linkages instead of preactivated functional groups as latent reactive sites. Nevertheless, it is still challenging to achieve freewheeling selectivity in the site of C−H modification. In 2019, a breakthrough that unveiled an efficacious and facile technique for crafting aryl thianthrenium salts via a site-specific C−H thianthrenation procedure was made by Ritter and colleagues[13] by pioneering extensive advancements in transformations centered around thianthrenium salts.[14] The subsequent conversions of these salts yield diverse C−H-activated aromatic products, thereby enriching the chemistry and chemical biology toolbox. Encouraged and inspired by related outstanding works and our continued interest in photocatalytic reactions,[15] we herein introduce a convenient method for the efficient arene $C(sp^2)$−H thiophosphorylation employing thianthrenium salts, , and diarylphosphine oxides under mild conditions (Scheme 1c). This strategy exhibits the non-necessity of metal involvement, remarkable site specificity, good substrate applicability and functional group tolerance, nontoxic and odorless S source, and wide applications in the late-stage functionalization of bioactive molecules.

Our investigation started with the examination of the model reaction between **1a**, **2a**, and **3a** under various reaction conditions (Table S1). As an initial attempt, the model reaction was conducted in the presence of photocatalyst **A** and CH_3CN as the solvent under irradiation of 455 nm LEDs. Delightfully, the reaction provided product **4a** in 53% yield (entry 1). Then, we tuned the experimental parameters to optimize the reaction conditions. Other photocatalysts (PCs), such as **B**, **C**, and **D**, resulted in yields lower than that of **A** (entries 2−4). The influence of different solvents, including DCM, toluene, and a mixed solvent was then examined (entries 5−7). The results showed that CH_3CN/DCM (9:1) was the best choice and afforded the desired product **4a** in a yield of 65%. Further investigation was performed on the anion of **1a**, and the reaction yield dramatically increased to 93% with a BF_4^- anion instead of TfO^- (entry 8). In addition, the reaction was carried out using the optimized reaction conditions in the absence of light. The transformation was severely inhibited, which demonstrates the important role of light in the reaction (entry 9). The following control experiment also revealed that the photocatalyst and inert gas atmosphere were indispensable for the reaction (entries 10 and 11).

With the optimal conditions in hand, the substrate of this strategy was explored. As presented in Scheme 2, the results revealed that the current strategy turned out to be a general and efficient method for the synthesis of thiophosphates. A series of thianthrenium salts were first examined to expand the synthesis utility of our proposed protocol. To our delight, both monosubstituted and multisubstituted aryl thianthrenium salts were able to participate well in the present transformation. Both electron-donating (MeO) and electron-withdrawing (COOMe, COMe, F, Cl, Br, and I) groups on the phenyl ring at the *para*-, *meta*- or *ortho*-position of the benzene ring of thianthrenium salts were tolerable and afforded the corresponding products in 71−85% yields (**4c**−**4h**). Steric hindrance was found to bring little influence on this reaction according to the phenomenon that the *ortho*-substituted thianthrenium salts (**4e**, **4f**, **4g**, and **4h**) delivered yields similar to those of their *meta*- or *para*-analogues. The trifluoromethoxy and difluoromethoxy groups, commonly encountered in drug molecules, are also tolerated with a high reaction efficiency in this system (**4j** and **4k**). Moreover, heterocyclic arene substrates were compatible under the standard conditions to give the corresponding thiophosphates, which demonstrated some potential possibility in functional molecule synthesis (**4x**, **4y**, and **4z**). To further assess the generality of this strategy, a broad range of phosphine oxides was then investigated (**4aa**−**4af**). As shown, various diarylphosphine oxides performed well in this system to provide the thiophosphorylation products in high yields (**4aa**−**4ac**). Furthermore, it is reassuring that phosphite esters, which frequently occur in pesticide molecules, as well as other reagents containing P(O)−H motifs, can effectively react with thianthrenium salts and DABSO to yield the corresponding P- and S-containing products (**4ad**−**4af**). Such a finding holds particular value for research in synthetic chemistry and pesticide science as it broadens our capability to construct complex molecular structures and may pave the way for the development of efficient and environmentally friendly pesticide production.

Notably, our following investigation on late-stage $C(sp^2)$−H modification of complex molecules revealed that an array of biologically significant compounds, including gemfibrozil, pyriproxyfen, famoxadone, pyriproxyfen, sildenafil, flurbiprofen, oxazolidinone, and etofenprox, demonstrated excellent compatibility within the described reaction process to offer the structurally modified end products (**4ag**−**4an**) with yields ranging from moderate to high (Scheme 2). These outcomes underscore the potential of our methodology as a powerful instrument for the meticulous late-stage modification of drug

Scheme 2. Substrate Scope for the Aromatic C−H Thiophosphorylation[a]



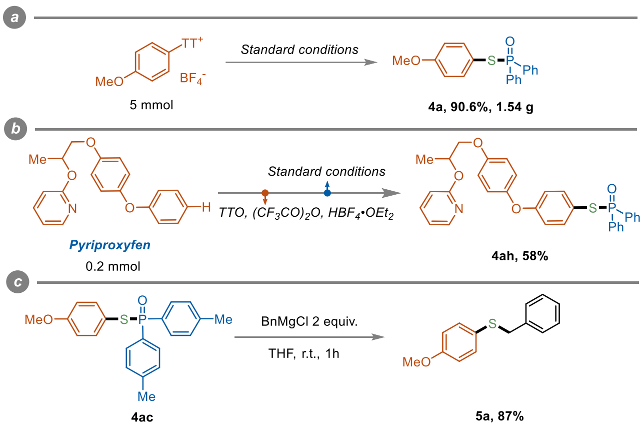
[a]Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), **3** (0.6 mmol), Mes-Acr-Me$^+$ClO$_4^-$ (**A**) (8 μmmol), and CH$_3$CN/DCM (9:1) (3.0 mL) under N$_2$ and irradiation of 30 W 455 nm LEDs for 24 h at 25 °C. [b]Isolated yield.

entities and intricate bioactive frameworks, thereby enhancing the scope of molecular tailoring in pharmaceutical and biochemical research.

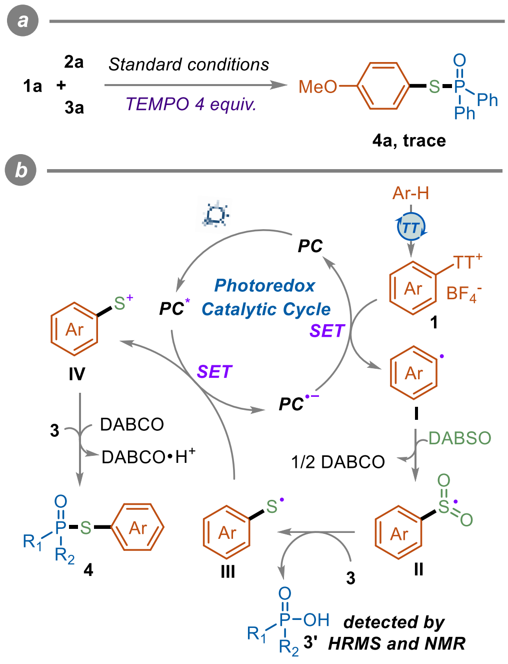
To further explore the potential of this approach in practical synthesis, a gram-scale experiment was conducted (Scheme 3a). Encouragingly, the reaction proceeded smoothly and delivered 1.54 g of **4a** in 90.6% yield after purification, thereby affirming the scalability and user-friendliness of our photochemical procedure. Of significance, the byproduct thianthrene was efficiently recovered and subsequently reused in the next cycle after complete oxidation, which highlights the sustainability aspect of the process. Furthermore, the valuable late-stage C−H thiophosphorylation of pyriproxyfen using a one-pot strategy was successfully achieved to produce the corresponding compound **4ah** in a reasonable two-step yield (Scheme 3b). Additionally, **4ac** could be conveniently converted into **5a** under mild conditions, which demonstrates potential application value in the green and odorless synthesis of sulfides (Scheme 3c).

To understand the possible mechanism of the reaction, a series of mechanistic experiments were carried out. Radical-trapping experiments were performed by adding 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) as a radical scavenger to the standard conditions (Scheme 4a). The formation of the desired product was almost inhibited, thereby reflecting the reaction to undergo a radical pathway. The light on−off experiment was performed next to demonstrate that continuous irradiation is essential for the reaction. To obtain

Scheme 3. Synthetic Applications



Scheme 4. Mechanistic Studies



detailed information about the initial electron transfer process, fluorescence quenching experiments were separately conducted between photocatalysts and substrates **1a**, **2a**, **3a**, 1,4-diazabicyclo[2.2.2]octane (DABCO), and 4-methoxyphenyl disulfide (**6**, precursor of radical **III**). As shown in Figures S2−S6, the 580 nm fluorescence launched by Mes-Acr-Me$^+$ClO$_4^-$ was observed when it was excited at 360 nm, and the stepwise addition of DABCO and **6** both dramatically quenched the fluorescence intensity while only a slight quenching was observed with **1a**. The Stern−Volmer fluorescence quenching plots presumably indicated a single-electron transfer between the excited state of Mes-Acr-Me$^+$ClO$_4^-$ and DABCO or **6** (Figure S7). Meanwhile, no significant fluorescence quenching phenomena were observed for compounds **2a** and **3a**.

Grounded in the experimental outcomes and prior literature,[14] a speculative reaction mechanism is outlined in Scheme 4c. The process commences with photoinduced single-electron transfer (SET) from the trace amount of DABCO from **2** to the photoexcited **PC*** under blue light. A following SET event between **1** and obtained **PC**$^{•-}$ spontaneously occurs, which results in the formation of an aryl radical **I** and regeneration of **PC**. The subsequent step sees aryl radical **I** being intercepted by DABSO to produce intermediate **II** and 1/2 molecule of DABCO. Subsequently, **3** can serve to reduce **II** to deliver sulfur radical **III**. Another SET process takes place between radicals **III** and **PC***, which leads to the creation of sulfur cation **IV**. Ultimately, **IV** electrophilically attacks **3** to provide product **4** after deprotonation by DABCO.

In conclusion, we have established a highly efficient visible-light-driven methodology for synthesizing thiophosphates via a three-component reaction involving aryl thianthrenium salts, DABCO·(SO$_2$)$_2$, and phosphine oxides. Our approach offers a straightforward route to consecutively construct C−S and S−P bonds starting from aryl C−H and P−H bonds directly. The introduced method exhibits metal-free and mild conditions, a broad substrate scope, remarkable functional group compatibility, and, therefore, some advancements in thianthrenium salt chemistry. Of critical importance, this strategy paves a promising way for late-stage C−H modifications of diverse bioactive molecules, thereby enhancing the prospects for drug/pesticide development.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

SI Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.4c02525.

Mechanism investigations; synthetic procedures; characterization data; and ^{1}H, ^{13}C, and ^{31}P NMR spectra of these synthesized compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Yunhe Jin − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China;* orcid.org/0000-0003-0626-4587;
Email: jinyh18@dlut.edu.cn

Authors

Ziyu Gan − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China;* orcid.org/0009-0005-0226-0572
Shuyang Liu − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China;* orcid.org/0009-0001-8246-4970
Jiajin Chen − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China*
Ziyang Chen − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China*
Yongqiang Zhang − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China*
Lifang Wang − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Han Wang − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Yihao Li − *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.orglett.4c02525

Notes

The authors declare no competing financial interest.

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