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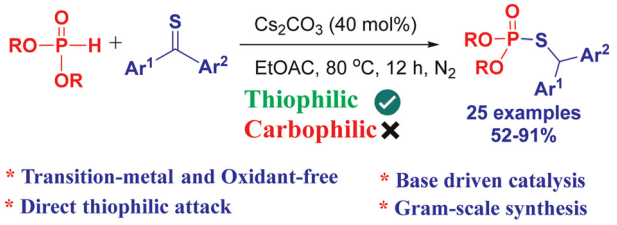

Cesium carbonate-catalyzed synthesis of phosphorothioates *via* *S*-phosphination of thioketones

Zu-Wei Chen, Annamalai Pratheepkumar, Rekha Bai, Yongyi Hu, Satpal Singh Badsara, Kuo-Wei Huang and Chin-Fa Lee*

A highly efficient and environmentally-friendly base-mediated transition metal-free direct thiophilic catalytic approach is reported for the synthesis of *S*-benzhydryl-phosphorothioates by reacting phosphite nucleophiles with diarylmethanethione.

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Cesium carbonate-catalyzed synthesis of phosphorothioates *via* *S*-phosphination of thioketones†

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A highly efficient and environmentally-friendly base-mediated transition metal-free direct thiophilic catalytic approach is reported for the synthesis of *S*-benzhydryl-phosphorothioates by reacting phosphite nucleophiles with diarylmethanethione. A wide variety of thioketones were coupled with different phosphite derivatives to provide the corresponding phosphorothioates in good to excellent yields. The control experiments and density functional theory (DFT) calculations rely on the regio-selective thiophilic addition of a phosphite nucleophile *via* umpolung protocols.

Organophosphorous compounds are omnipresent building blocks of various organic frameworks[1] and have potential applications in synthetic chemistry,[2] agrochemicals,[3] and pharmaceuticals.[4] Phosphorothioates are a class of organophosphorus compounds that have ubiquitous advantages in the field of pesticides,[5] bioactive molecules,[6] and materials science.[7] Phosphorothioate-modified oligonucleotides have shown potential applications as RNA-targeted therapeutics,[8] HIV-I inhibitors,[9] and anticholinesterase inhibitors.[10] The synthetic utility and pharmaceutical applications of phosphorothioates and organo-thiophosphorous compounds have always attracted the scientific community to develop synthetic methodologies for these types of compounds.[11] Early-stage development and traditional methods for the phosphorothioates are often hampered by the pre-functionalization of phosphorous derivatives and various thiol surrogates, associated with harsh reaction conditions, toxicity, and moisture sensitivity.[12] In recent years, transition metal-catalyzed,[13] electrochemical synthesis,[14] photo-redox catalysis,[15] and metal-free[16] approaches using various phosphorous and sulfur surrogates have been developed for synthesizing phosphinothioates or phosphorothioate compounds.

Meanwhile, Brook rearrangement[17] and further advancements like aza-Brook,[18] bora-Brook,[19] and phospha-Brook[20] rearrangements were successfully employed for the synthesis of simple or complex organic molecules. In particular, thioketones are widely chosen for the synthesis of various organic frameworks due to the unique properties of the C=S bond compared to the C=O bond, such as high reactivity of the C=S bond, the larger atomic radius of the sulfur atom, strong electrophilicity, the higher HOMO orbitals, and the lower LUMO orbitals (Scheme 1a).[21] The pioneering studies of Beak *et al.* uncovered the reactivity pattern of thioketones and developed a synthetic protocol for the synthesis of benzhydryl phenyl sulfide from the coupling of diarylthioketone and phenyl lithium at room temperature (Scheme 1b).[22] Takeda *et al.* have developed a reaction between silyl thioketone and lithium diethyl phosphite at −98 °C to afford a thiophilic attacked product as a major product, whereas *S*-attacked and thia-Brook rearranged products were found as minor products (Scheme 1c).[23] However, these protocols showed some limitations and drawbacks such as limited substrate applicability, safety issues, and harsh reaction conditions required for the completion of the reactions. For the above-mentioned reasons, an environmentally friendly, atom-economical, and mild reaction condition protocol for the preparation of phosphorothioates is still desired in this field. In our endeavor to develop efficient synthetic methodologies for the organo-thiophosphorus compounds,[14,24] herein, we disclose a novel, regioselective, and efficient catalytic protocol for the synthesis of *S*-benzhydryl phosphorothioates *via* direct thiophilic attack of phosphite nucleophiles, which afforded a broad spectrum of phosphorothioate compounds.

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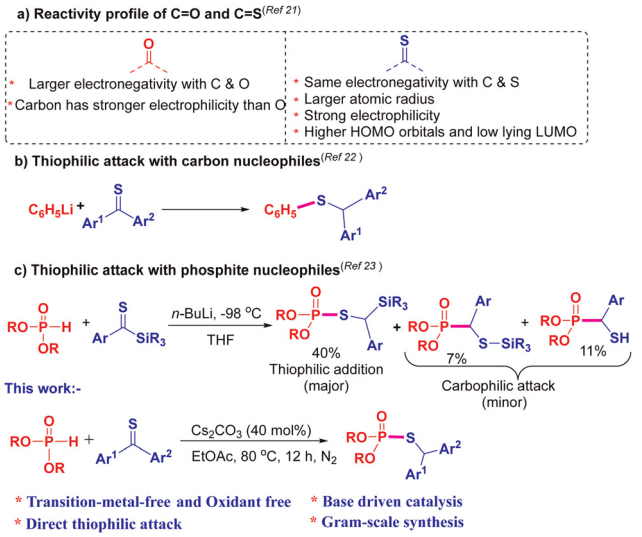
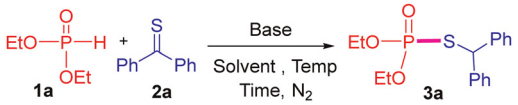
† Electronic supplementary information (ESI) available. CCDC 2183574. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2cc04331a



Scheme 1 Synthetic utilization of thioketones and phosphorous nucleophiles.

In our initial investigations, a reaction was carried out with commercially available diethyl phosphites (**1a**) and diphenylmethanethione (**2a**) in the presence of Et_3N (40 mol%) in ethyl acetate at 80 °C for 12 h, which underwent thiophilic *S*-attack to afford the desired phosphorothioate **3a** in a 64% isolated yield (Table 1, entry 1). A reaction without a base did not give the desired product, which emphasizes the catalytic role of the base (Table 1, entry 2). Only a trace amount of **3a** was detected when nucleophilic base DABCO was used instead of triethylamine (Table 1, entry 3). The other non-nucleophilic bases such as CsF, K_2CO_3, and Na_2CO_3 gave moderate yields of **3a** (39–48%) (Table 1, entries 4–6). Gratifyingly, cesium carbonate increased the reactivity and provided *S*-benzhydryl phosphorothioate **3a** in an 86% yield (Table 1, entry 7). Both, reducing and increasing the time of the reaction diminished the yield of **3a** (Table 1, entries 8 and 9).

Table 1 Optimization of the reaction conditions[a]



Entry	Base	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1.	Et_3N	EtOAc	80	12	64
2.	—	EtOAc	80	12	N.R.
3.	DABCO	EtOAc	80	12	Trace
4.	CsF	EtOAc	80	12	39
5.	K_2CO_3	EtOAc	80	12	48
6.	Na_2CO_3	EtOAc	80	12	43
7.	Cs_2CO_3	EtOAc	80	12	86
8.	Cs_2CO_3	EtOAc	80	6	45
9.	Cs_2CO_3	EtOAc	80	18	83
10.	Cs_2CO_3	EtOAc	100	12	84
11.	Cs_2CO_3	DMF	80	12	25
12.	Cs_2CO_3	1,4-Dioxane	80	12	68
13.	Cs_2CO_3	Toluene	80	12	85
14.	Cs_2CO_3	EtOH	80	12	71
15.[c]	Cs_2CO_3	EtOAc	80	12	84
16.[d]	Cs_2CO_3	EtOAc	80	12	42
17.[e]	Cs_2CO_3	EtOAc	80	12	38

[a] Reaction conditions: diethyl phosphites (**1a**) (0.3 mmol), diphenylthioketone (**2a**) (0.45 mmol), base (40 mol%), and solvent (2.0 mL) under a N_2 atmosphere. [b] Isolated yield based on **1a**. [c] 50 mol% Cs_2CO_3 was used. [d] 30 mol% Cs_2CO_3 was used. [e] 20 mol% Cs_2CO_3 was used.

For further enhancement in the yield, the temperature and solvents were also screened. Increasing the reaction temperature up to 100 °C did not notably affect the product yield (Table 1, entry 10). In the toluene solvent system, product **3a** was observed in an 85% yield, whereas other solvent systems (DMF, 1,4-dioxane, and EtOH) were not found to be superior to ethyl acetate (Table 1, entries 11–14). It is worth mentioning here that increasing the amount of Cs_2CO_3 from 40 mol% to 50 mol% provided similar results (Table 1, entry 15), whereas decreasing the amount of Cs_2CO_3 gave inferior results (Table 1, entries 16 and 17).

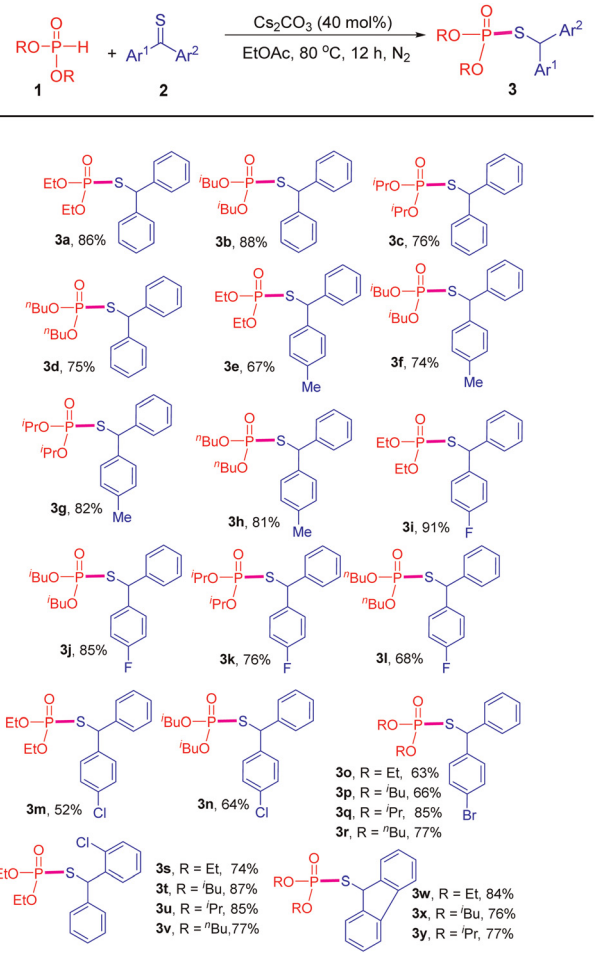
With the robust conditions in hand, to check the generality of the developed protocol, various thiophilic *S*-attack-mediated phosphorothioates **3a–y** were synthesized in 52–91% yields (Table 2). Phosphites **1a–d** contained different substituents (Et, ^{i}Pr, ^{i}Bu, and ^{n}Bu) coupled with diaryl thioketone **2a**, which gave the corresponding *S*-benzhydryl phosphorothioates **3a–d** in 75–88% yields.

Thioketone **2b** possessing electron-donating groups (EDGs) coupled with phosphites **1a–d** providing the corresponding phosphorothioates **3e–h** in 67–82% yields. The halogen (F, Cl, and Br)-containing diaryl thioketones smoothly reacted with different phosphite nucleophiles under the optimized reaction conditions and afforded the corresponding phosphorothioates **3i–v** in 52–91% yields. Phenyl(*p*-fluoro)methanethione **2c** coupled well with phosphites **1a–d** to provide the phosphorothioate products **3i–l** in 68–91% yields. Similarly, *p*-(chloro and bromo)-substituted diaryl thioketones **2d and e** showed efficient reactivity towards various phosphites **1a–d** for the synthesis of phosphorothioate compounds **3m–3r** in 52–85% yields. Notably, sterically hindered phenyl(*o*-chloro) methanethione substrate **2f** also reacted well with various phosphites **1a–d** and gave the corresponding phosphorothioates **3s–v** in 74–87% yields. Thioketone 9*H*-fluorene-9-thione **2g** also showed good reactivity with phosphites **1a–1c** to give the phosphorothioates **3w–y** in 76–84% yields. Compounds **3a–y** were all well characterized by ^{1}H and ^{13}C NMR spectral data and HRMS data, and the structure of compound **3p** was further confirmed by single-crystal data analysis.[25] However, thioketones, 1-phenylethane-1-thione (**2h**), benzothioamide (**2i**), *O*-methyl benzothiate (**2j**) and 2*H*-chromene-2-thione (**2k**) (Fig. 1) could not undergo the *S*-phosphination process under the standard reaction conditions.

To demonstrate the practicability and synthetic applicability of the developed protocol, a gram-scale experiment was performed *via* the reaction between **1a** and **2a** following the standard conditions, which afforded product **3a** in 81% (1.37 g) isolated yield (Scheme 2).

To gain insight about the reaction pathway of the developed regioselective P–S bond synthesis protocol, we carried out some

Q7 Table 2 Substrate scope of phosphonates and thioketones[a]



[a] Reaction conditions: phosphites **1** (0.3 mmol), thioketones**2** (0.45 mmol), Cs_2CO_3 (40 mol%), and ethyl acetate (2 mL) under N_2 at 80 °C for 12 h. Isolated yields based on **1**.

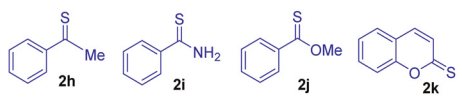
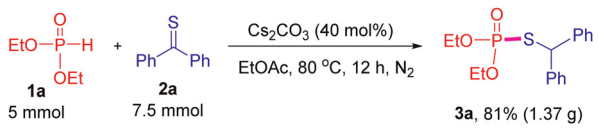
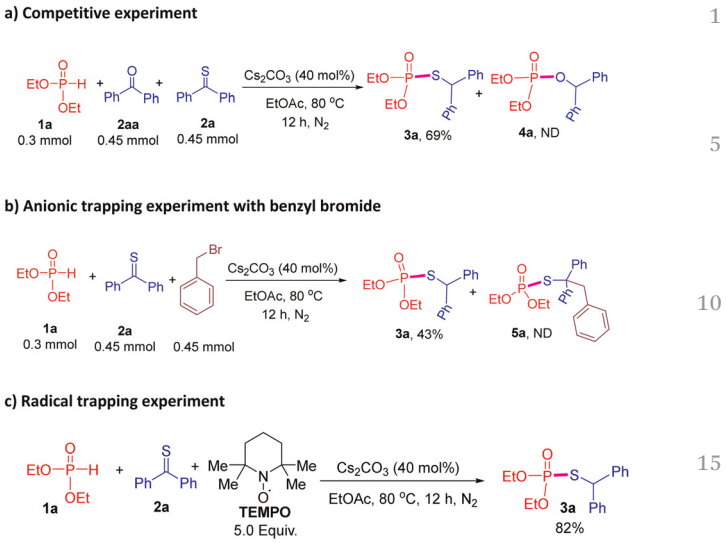


Fig. 1 Unsuccessful substrates.

control experiments with different substrates (Scheme 3). A competitive experiment between benzophenone (**2aa**) and diphenylmethanethione (**2a**) with diethyl phosphonate (**1a**) was carried out to check the product selectivity and feasibility. Interestingly, it regioselectively gave rise to phosphorothioates **3a** in 69% isolated yield without the detection of **4a**



Scheme 2 Gram-scale synthesis.



Scheme 3 Control experiments. Q8

(Scheme 3a). Subsequently, an anionic trapping experiment with the use of benzyl bromide was performed and it gave rise to product **3a** without the detection of any benzyl bromide coupled product **5a** (Scheme 3b). Furthermore, the reaction between **1a** and **2a** in the presence of 5.0 equiv of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl; a radical scavenger) provided the desired product **3a** in 82% yield (Scheme 3c). This radical trapping experiment ruled out the possible radical pathway for this *S*-phosphination protocol.

Based on the above-mentioned observations, the literature and supported by density functional theory (DFT) calculations (see ESI†), a plausible reaction mechanism was proposed by taking **1a** and **2a** as model substrates (Fig. 2). Initially, phosphite **1a** interacts with Cs_2CO_3 and transforms into cesium-stabilized phosphite anion **I** with the formation of $CsHCO_3$. Anion **I** further undergoes thiophilic addition onto thioketone **2a** *via* kinetically favorable transition state **TS_S** to give the carbanion species, intermediate **II**. Upon protonation, *S*-benzhydryl phosphorothioate **3a** can be formed. The regenerated Cs_2CO_3 again participates in the catalytic cycle.

In conclusion, for the first time, we have developed a practically-scalable, efficient and environment-friendly base-mediated, transition metal-free and oxidant-free direct thiophlic catalytic approach for the synthesis of *S*-benzhydryl phosphorothioates. This conventional base-assisted protocol was found to be useful for the synthesis of a wide variety of phosphorothioates by employing a variety of thioketones with phosphite derivatives containing electron-donating as well as electron-withdrawing groups in good yields. The control experiments and density functional theory (DFT) calculations rely on the regioselective thiophilic addition of a phosphite nucleophile *via* umpolung protocols.

This work was financially supported by the Ministry of Science and Technology, Taiwan (Most 110-2113-M-005-014-MY3), National Chung Hsing University, i-Center for Advanced Science and Technology (iCAST), the "Innovation and Q9

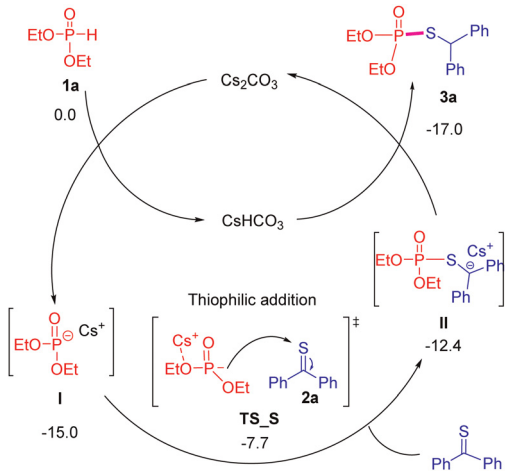


Fig. 2 Plausible reaction mechanism with single point energies under B3LYP(IEFPCM, EA)/6-31 + +G(d,p)/SDD || B3LYP/6-31G(d)/SDD in kcal mol^{-1}.

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Conflicts of interest

■■■■

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25 CCDC-2183574 (3p) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via **www.ccdc.cam.ac.uk/data_request/cif**.

