



Cite this: *RSC Adv.*, 2024, 14, 32200

Received 22nd June 2024
Accepted 25th September 2024

DOI: 10.1039/d4ra04568h

rsc.li/rsc-advances

A facile, catalyst- and additive-free, and scalable approach to the photochemical preparation of disulfides from organosulfenyl chlorides†

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A novel, clean and efficient protocol for the preparation of disulfides has been developed through the photochemical radical homo- and cross-coupling reaction of sulfenyl chlorides under LED irradiation and without the use of any catalyst and additive. The representative photochemical homo-coupling of trichloromethyl sulfenyl chloride has been successfully conducted on kilogram-scale in a continuous flow mode. The solvent and the main byproduct can be recovered in high yields, which makes the approach be highly atom economical.

Introduction

Disulfides are widely used in biological studies and material science. For example, the disulfide unit often plays a key role for the formation and stabilization of the 3D structure of polypeptides and proteins in diverse biochemical processes.¹ A disulfide derivate can also be promisingly served as the linker to form an antibody-drug conjugate by attaching a chemical probe, an imaging agent or a drug to a biomolecule.² In fact, many biologically active natural products, pharmaceuticals and agrochemicals contain disulfide moieties.^{3,4} In addition, disulfides are often known as popular rubber additives (Fig. 1).⁵ Due to its wide application, a plethora of synthetic methods to access disulfides have been reported.

The most common method for the preparation of symmetrical disulfides is through the oxidative coupling of thiols. Various oxidizing agents such as air, iodine, hydrogen peroxide and chromates have been successfully applied to this transformation with the help of a metal or metal-free catalyst (Scheme 1a).⁶ The nucleophilic substitution of S–H bonds (Scheme 1b),⁷ the reductive coupling of sulfonyl chlorides, thiosulfonates and thiosulfates, and the reductive dimerization of thiocyanates and ethoxythio have also been utilized for the preparation of symmetrical disulfides (Scheme 1c).⁸ More recently, Wu & Tang *et al.* reported a radical pathway towards the synthesis of symmetrical disulfides from thiols catalyzed by an environmentally friendly catalyst zeolite ETS-10 in the

absence of oxidants and additives (Scheme 1d).⁹ Although in some special cases, an unsymmetrical disulfide can become the main product of coupling reactions between two different thiols, the chemoselective approaches for the synthesis of unsymmetrical disulfides have recently received extensive attention since more diverse disulfide products could be expected. The metal-catalyzed cross-coupling or nucleophilic substitution approaches with prefunctionalized/activated disulfurating reagents (RSS-LG) have proven effective for constructing unsymmetrical disulfides (Scheme 1e).¹⁰ The unsymmetrical disulfides have also been obtained *via* a catalytic disulfide exchange reaction (Scheme 1f).¹¹ Lei *et al.* reported a facile oxidant- and catalyst-free electrochemical method for the cross-coupling of an aryl mercaptan with an alkyl mercaptan

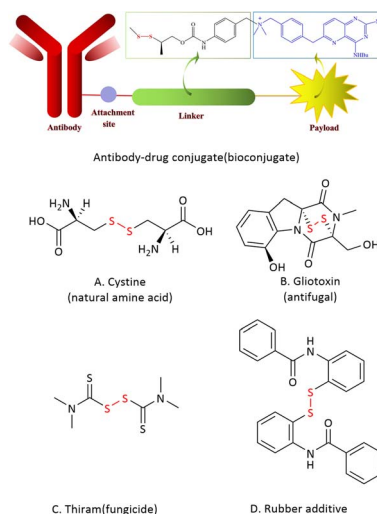


Fig. 1 Representative disulfides and their applications.

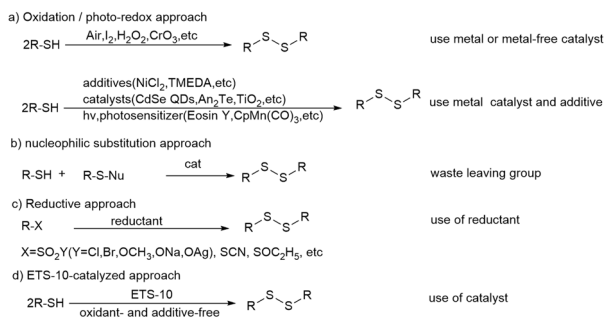
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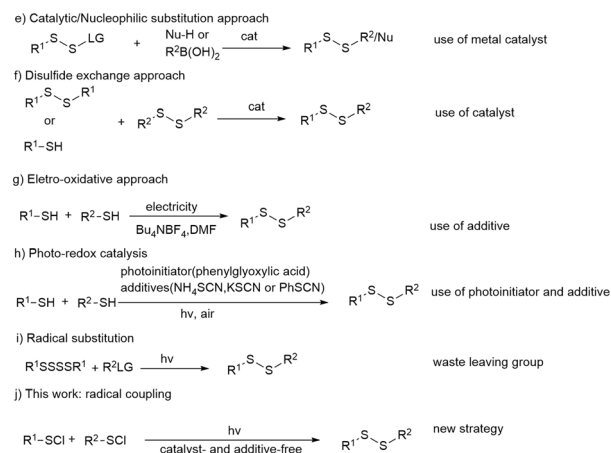
† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ra04568h>



Symmetrical disulfide preparation approach



Unsymmetrical disulfide preparation approach



Scheme 1 Approaches for the synthesis of disulfides.

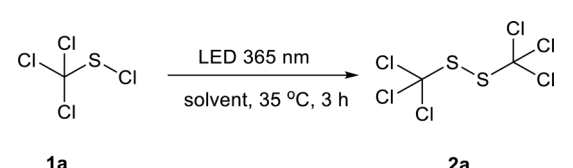
by utilizing $n\text{-Bu}_4\text{NBF}_4$ as the electrolyte (Scheme 1g).¹² On the other hand, as an environmentally friendly alternative to the conventional synthetic chemistry, photochemistry has recently attracted much attention.¹³ Photochemical protocols have also been successfully employed for the preparation of disulfides. Different metal and metal-free photocatalysts have been used for the synthesis of both symmetrical and unsymmetrical disulfides from different thiols (Scheme 1h).¹⁴ In addition, Wu & Parrr reported a simple and effective approach for the preparation of unsymmetrical disulfides through the radical substitution on tetrasulfides with the help of a photocatalyst and blue LED irradiation (Scheme 1i).¹⁵ A broad range of unsymmetrical disulfides were obtained in acceptable yields. Although great success has been achieved in the synthesis of disulfides, they are usually associated with some drawbacks such as the use of metal catalysts, photocatalysts and/or environmentally harmful additives.¹⁶ Herein, we report the synthesis of disulfides through a photochemical homo/cross-radical coupling reaction of organosulfonyl chlorides without the use of any catalyst, oxidant/reductant and other additives (Scheme 1j). The reaction can be performed both in a batch and a continuous-flow mode. Both the solvent and main byproduct can be effectively recovered by distillation. Although the synthesis of organosulfonyl chlorides is not usually so “green”, this new protocol provides an alternative choice for researchers in related fields.

Results and discussion

Initially, the photochemical reaction of trichloromethyl sulfonyl chloride **1a** in water was conducted under LED irradiation at 365 nm. Gratifyingly, the reaction proceeded smoothly and the desired product 1,2-bis(trichloromethyl)disulfide **2a** was obtained in a moderate yield of 46% (Table 1, entry 1). Encouraged by this result, various solvents were then screened. Methanol, ethanol and isopropanol improved the disulfide yields to 82%, 80% and 74%, respectively (Table 1, entries 2–4). Whereas acetic acid (CH_3COOH) was inferior and gave a relatively lower yield of 50% (Table 1, entry 5). No product was detected when the reaction was conducted in chloroform (CHCl_3) (Table 1, entry 6). Acetonitrile (CH_3CN), benzene and toluene were also applicable for this reaction, affording the desired product in a yield of 76%, 79% and 75%, respectively (Table 1, entries 7–9). The employment of n -pentane gave **2a** in an excellent yield of 90% (Table 1, entry 10), while cyclohexane was found to be the best one among the solvents screened with the highest yield of 92% at 365 nm (Table 1, entry 11).

A short reaction time of 15 minutes was found to be enough to furnish the reaction (Table 2, entries 1–5). The effect of irradiation wavelength in the range of 350 nm to 455 nm was then investigated. The disulfide yield increased firstly with increasing wavelength, and an excellent isolated yield of 93% was achieved at 405 nm (Table 2, entries 6–8). The light irradiation at the wavelengths of 420 and 455 nm led to decreased yields of 81% and 75% respectively (Table 2, entries 9–10). Further screening on the reaction temperature revealed that either decreasing the temperature to 25 °C (Table 2, entry 11) or elevating it to 45 °C (Table 2, entry 12) did not improve the reaction yield. Therefore, the best reaction conditions were established as follows: irradiating **1a** in cyclohexane with a LED of 405 nm at 35 °C for 15 minutes (Table 2, entry 8).

Table 1 Solvent screening for the photocatalytic coupling reaction^a

		
Entry	Solvent	Yield ^b (%)
1	H ₂ O	46
2	Methanol	82
3	Ethanol	80
4	Isopropanol	74
5	CH ₃ COOH	50
6	CHCl ₃	0
7	CH ₃ CN	76
8	Benzene	79
9	Toluene	75
10	n -Pentane	90
11	Cyclohexane	92

^a Reaction conditions: **1a** (50 mmol), solvent (53 mL), 35 °C, 365 nm LED, 3 hours. ^b Determined by GC area normalization method.



Table 2 Optimization of the photocatalytic coupling reaction conditions^a

Entry	Wavelength (nm)	Temp. (°C)	Time (min)	Yield ^b (%)
1	365	35	120	92
2	365	35	60	92
3	365	35	30	92
4	365	35	15	92
5	365	35	10	90
6	350	35	15	62
7	385	35	15	93
8	405	35	15	96 (93 ^c)
9	420	35	15	81
10	455	35	15	75
11	405	25	15	90
12	405	45	15	92

^a Reaction conditions: 50 mmol **1a**, cyclohexane (53 mL), LED.^b Determined by GC area normalization method. ^c Isolated yield.

With the optimized conditions in hand, the scope of various sulfenyl chlorides was investigated (Scheme 2). To our delight, expected symmetrical disulfides were obtained in good to excellent yields for various substituted phenyl sulfenyl chlorides. 1,2-bis(phenyl)disulfide (**2b**) was produced from phenyl sulfenyl chloride with a good yield of 73%. 4-Bromo-substituted phenyl sulfenyl chloride gave the corresponding product (**2c**) in a similar yield. All of the phenyl sulfenyl chlorides with a strong electron-withdrawing group of trifluoromethyl at the *ortho*-, *meta*- or *para*-position of the benzene ring generated the

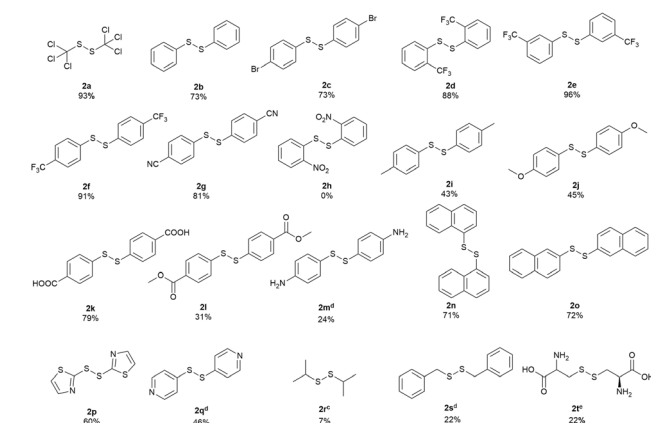
corresponding products with excellent yields (**2d**: 88%, **2e**: 96% and **2f**: 91%, respectively). While the 4-cyanophenyl sulfenyl chloride delivered the product smoothly with a good yield of 81% (**2g**), the 2-nitrophenyl sulfenyl chloride failed in the reaction (**2h**), which might due to the existence of the photo-sensitive nitro group.¹⁷ The substrates with an electron-donating substitute (–Me and –OMe) on the benzene ring were applicable to this reaction with moderate product yields (**2i** and **2j**). 4,4'-disulfanediylidibenzoic acid (**2k**) and dimethyl 4,4'-disulfanediylidibenzoate (**2l**) were prepared from corresponding sulfenyl chlorides with a yield of 79% and 31% respectively. When 4-amine phenylsulfenyl chloride was applied, a salt-like solid mixture containing 24% of 4,4'-disulfanediylidianiline (**2m**) according to HPLC analysis (area normalization method) was obtained. Both naphthalen-1-yl sulfenyl chloride and naphthalen-2-yl sulfenyl chloride could give corresponding products in good yields (**2n** & **2o**). Furthermore, the heterocyclic compound thiazol-2-yl sulfenyl chloride reacted smoothly to generate 1,2-di(thiazol-2-yl)disulfide (**2p**) in a moderate yield of 60%. In contrast, pyridyl sulfenyl chloride produced a salt-like solid containing 46% of 1,2-bis(4-pyridyl)disulfide (**2q**). When isopropyl sulfenyl chloride was used, a mixture of 1,3-bis(isopropyl)trisulfide (main product), 1,2-bis(isopropyl)disulfide (**2r**) and isopropyl sulfide was obtained. Benzylic sulfenyl chloride gave a mixture of 1,2-bis(benzyl)disulfide (**2s**) with other impurities. *S*-chlorocysteine also gave a salt-like solid containing corresponding disulfide product (**2t**) of 22%.

Encouraged by the success in the homo-coupling of sulfenyl chlorides, the cross-coupling reaction between two different sulfenyl chlorides was then investigated. The reaction conditions were screened by the model reaction between trichloromethyl sulfenyl chloride (**1a**) and phenyl sulfenyl chloride (**1b**). The impact of different molar ratios and irradiation wavelength in the range of 350–455 nm was investigated (Table 3). To our delight, 1-phenyl-2-(trichloromethyl)disulfide (**2ab**) was obtained in a moderate yield of 49% with a molar ratio of 2 : 1 (**1a** : **1b**) under the 405 nm LED irradiation (Table 3, entry 3).

Subsequently, the cross-coupling of trichloromethyl sulfenyl chloride (**1a**) with different aryl sulfenyl chlorides and hetero-aryl sulfenyl chlorides were investigated (Scheme 3). The aryl sulfenyl chlorides bearing both an electron-withdrawing group (**1d**, **1f** & **1g**) and an electron-donating group (**1i**) on the benzene ring were applicable in this transformation. 1-(Naphthalen-2-yl)-2-(trichloromethyl)disulfide (**2ao**) and 2-((trichloromethyl)disulfaneyl)benzo[*d*]oxazole (**2au**) were also obtained in a moderate yield of 45% and 39%, respectively.

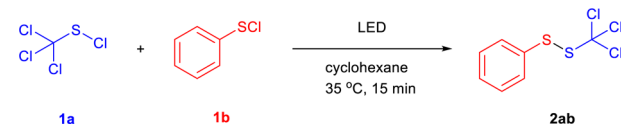
Next, the cross-coupling between phenyl sulfenyl chloride (**1b**) and other aryl sulfenyl chlorides was explored (Scheme 4). Several unsymmetrical diaryl disulfides, such as **2bc**, **2bf** and **2bi** were achieved in moderate yields of 40–50%.

To establish the mechanism of the reaction, a series of control experiments were performed (Scheme 5). It was found that the product yield was not affected when the reaction was conducted under a nitrogen or argon atmosphere (Scheme 5a). When the oxygen free radical scavenger benzoquinone was added, the reaction went smoothly and a product yield of 92%



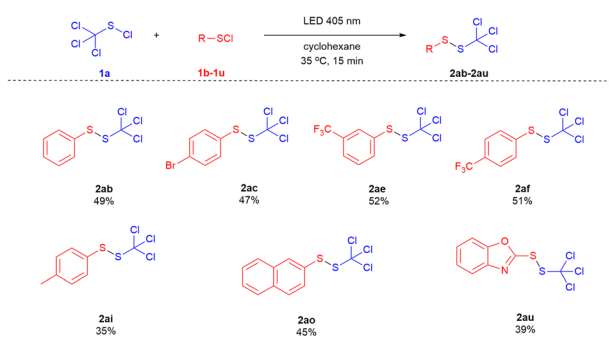
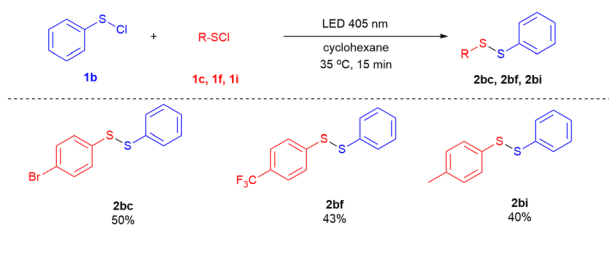
Scheme 2 Substrate scope of symmetrical disulfides. ^a Reaction conditions: substrate (5 mmol), cyclohexane (5.3 mL), LED 405 nm, 35 °C, 15 minutes. ^b Isolated yield. ^c Determined by GCMS. ^d Determined by HPLC (254 nm) area normalization method. ^e Determined by HPLC (210 nm) area normalization method.



Table 3 Reaction conditions screening of cross-coupling between trichloromethyl sulfonyl chloride and phenyl sulfonyl chloride^a


Entry	Molar ratio (1a : 1b)	Wavelength/nm	Yield ^b (%)
1	1.0	405	31
2	1.5	405	42
3	2.0	405	49
4	2.5	405	50
5	2.0	350	19
5	2.0	365	40
7	2.0	385	40
8	2.0	420	46
9	2.0	455	15

^a Reaction conditions: **1b** (1 mmol), cyclohexane (3.3 mL), 405 nm LED, 35 °C, 15 minutes. ^b Isolated yield base on **1b**.

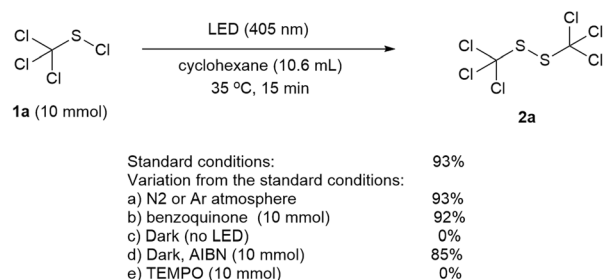
**Scheme 3** Cross coupling between trichloromethyl sulfonyl chloride (**1a**) and different sulfonyl chlorides.^{a,b} ^a Reaction conditions: substrate (1 mmol), **1a** (2 mmol), cyclohexane (3.3 mL), LED 405 nm, 35 °C, 15 minutes. ^b Isolated yield base on the aryl sulfonyl chloride (R–SCl).**Scheme 4** Cross coupling between phenyl sulfonyl chloride (**1b**) and other aryl sulfonyl chlorides.^{a,b} ^a Reaction conditions: **1b** (2 mmol), aryl sulfonyl chloride (1 mmol), cyclohexane (3.3 mL), LED 405 nm, 35 °C, 15 minutes. ^b Isolated yield base on R–SCl.

was obtained (Scheme 5b), implying that oxygen did not play a dominant role in this transformation. No product was detected without the LED irradiation (Scheme 5c). While the addition

of 2,2'-azobis(2-methylpropionitrile) (AIBN) under dark condition made the reaction proceed successfully with a product yield of 85% (Scheme 5d), the presence of free radical inhibitor TEMPO upon LED irradiation could completely block the reaction (Scheme 5e), which indicating that a radical pathway was involved in this transformation. In addition, the GC-MS analysis of the model reaction mixture under optimized conditions showed the presence of chlorocyclohexane (main byproduct), cyclohexyl(trichloromethyl)sulfide (minor byproduct) and trace of chloroform and 1-cyclohexyl-2-(trichloromethyl)-disulfide. Persistent emission of hydrogen chloride with slight chlorine gas was also detected with a pH test paper and a potassium iodide starch test paper.

Based on the experimental evidences and the literature report,¹⁸ a plausible reaction mechanism was proposed as shown in Scheme 6. The photochemical cleavage of trichloromethyl sulfonyl chloride **1a** under 405 nm LED irradiation generates the thiyl radical **E** and a chlorine radical. The homo-coupling of thiyl radical **E** produces the desired product 1,2-bis(trichloromethyl)disulfide **2a**. The hydrogen atom transfer (HAT) process between cyclohexane and chlorine radical gives the cyclohexyl radical **F**,¹⁹ which further undergoes a cross-coupling with chlorine radical to produce the main byproduct chlorocyclohexane **4**, indicating that the solvent cyclohexane simultaneously plays the role of a sacrificial reagent. A minor amount of chlorine radical is annihilated to form the byproduct chlorine gas. Cyclohexyl(trichloromethyl)sulfide **5** is generated by **E** and **F**. The photochemical cleavage of **5** affords the radical **G** and **H**, which can further produce chloroform **6**, and 1-cyclohexyl-2-(trichloromethyl)disulfide **7** through a HAT process and a radical cross-coupling reaction, respectively.

On the other hand, over the last decade, the continuous flow photochemistry has increasingly attracted attention from researchers both in academia and industry.²⁰ As the distribution of photons becomes more problematic with increasing reactor dimensions due to the attenuation effect of photon transport, photochemical transformation in flow mode can facilitate the photochemical processes and their subsequent scale-up due to the uniformly irradiation on the reaction mixture.²¹ The photochemical homo-coupling of trichloromethyl sulfonyl chloride **1a** was therefore investigated in flow mode with a Corning G1 reactor equipped with a tail gas absorber using water as the absorbent. After the optimization on the residence time and reaction temperature (see ESI, Table S1†), the best

**Scheme 5** Control experiments.

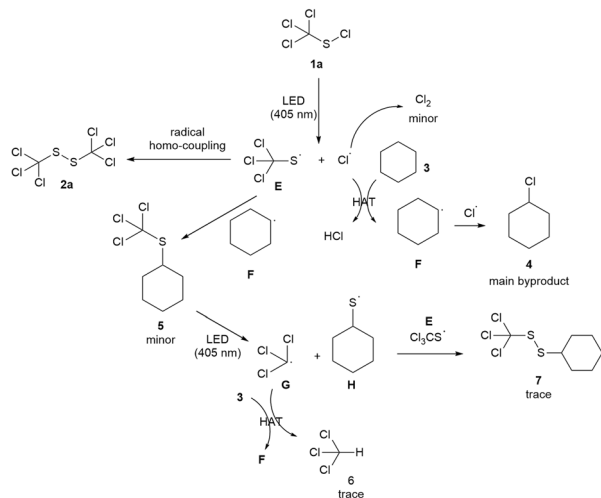
Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no conflicts.

Notes and references



Scheme 6 A plausible mechanism.

continuous flow reaction conditions were obtained as follows: **1a** in cyclohexane (0.85 M, 13.7 mL min⁻¹), 85 °C, 405 nm LED, residence time 3 minutes.

The photochemical homo-coupling of trichloromethyl sulfenyl chloride **1a** was then continuously run for more than 12 hours. After separating both the solvent cyclohexane and the main byproduct chlorocyclohexane out from the reaction mixture by distillation, 1410 g homo-coupling product **2a** (93.7% in yield) was obtained in a purity of 99.0% (GC area normalization method). Meanwhile, through an atmospheric and then vacuum distillation process, 7276 g cyclohexane in a purity of 99.6% (GC area normalization method) was recovered in a recovery of 96.1% by the conventional distillation, and the main byproduct chlorocyclohexane, which is a useful organic intermediate for the synthesis of rubber additives, was then obtained in a yield of 99.5% (1200 g) and in a purity of 98.3% (GC area normalization method) by the vacuum distillation. The recovered cyclohexane was reused in the next run and **2a** was achieved in the same yield (93.8%) (see ESI[†], solvent reuse experiment).

Conclusions

In summary, we have demonstrated a facile and clean protocol for the synthesis of both symmetrical and unsymmetrical disulfides from sulfenyl chlorides in moderate to excellent yields under the LED irradiation. The photochemical radical coupling reaction of sulfenyl chlorides was performable for a variety of aryl sulfenyl chlorides bearing both electron-donating and withdrawing substituents in the absence of any catalyst, oxidant/reductant and other additive in 15 minutes. The reaction can be scaled up to kilogram scale in a continuous-flow mode. The solvent as well as the main byproduct can be recovered in high yields, which makes the process be highly atomic economical. The recovered solvent can be reused without any negative effect on the reaction. Thus, the present work provides an efficient, eco-friendly, and scalable method for the preparation of disulfides.

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