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Highly selective cross-coupling reactions of 1,1-dibromoethylenes with alkynylaluminums for the synthesis of aryl substituted conjugated enediynes and unsymmetrical 1,3-diynes†

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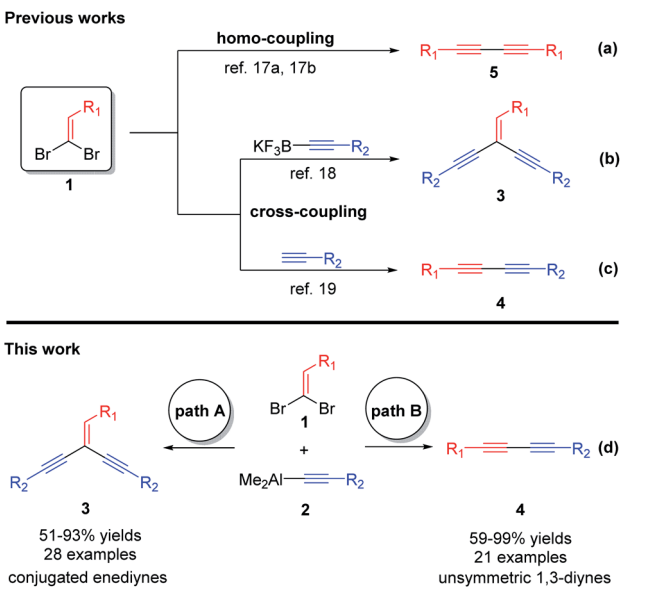
A highly efficient method for the synthesis of aryl substituted conjugated enediynes and unsymmetrical 1,3-diynes *via* selective cross-coupling reactions of 1,1-dibromoethylenes with alkynylaluminums using the $Pd(OAc)_2$–DPPE and $Pd_2(dba)_3$–TFP complexes as catalysts, respectively, has been successfully developed. Though the alkyl substituted conjugated enediynes and unsymmetrical 1,3-diynes were not obtained, this case is also remarkable as the same starting materials could selectively produce either aryl substituted conjugated enediynes or unsymmetrical 1,3-diynes in moderate to excellent yields (up to 99%) in the different Pd–phosphine catalytic systems.

Introduction

The conjugated enynes[1] and diynes,[2] which play important roles in organic synthesis, have been widely used in the preparation of natural products,[3] pharmaceuticals[4] and advanced materials.[5] Particularly, the conjugated enediynes are usually used for synthesis of electronic and optical materials.[6] Meanwhile, the 1,3-diynes are common structural motifs found in biologically active and pharmaceutical compounds, which are known to have anti-HIV,[7] anticancer,[8] antibacterial,[9] and anti-inflammatory properties.[10] Though several kinds of typical synthetic processes, including homo-[11] or cross-coupling,[12,13] diynone decarbonylation,[14] oxidative coupling[15] and oxidative decarboxylative homo-coupling,[16] have been realized, developing some efficient methods for accessing such frameworks from easily available organic compounds is very desirable and important.

The 1,1-dibromoethylenes, which are readily available from aldehydes, have attracted some attention due to their potentialities in the construction of conjugated enediynes and 1,3-diynes. Compared with the mature cases for constructing of symmetric conjugated 1,3-diynes, which are mostly from homo-coupling of 1,1-dibromoethylenes (Scheme 1a),[17] the applications of 1,1-dibromoethylenes for synthesizing of conjugated enediynes and unsymmetrical 1,3-diynes are very rare. In 2005, Kabalka *et al.* reported a highly efficient Suzuki–Miyaura coupling of 1,1-dibromo-1-olefin with potassium alkynyl trifluoroborate to provide conjugated enediynes (Scheme 1b).[18] Besides, they have been successfully applied to the cross-coupling reaction of terminal alkynes to produce unsymmetrical conjugated 1,3-diynes (Scheme 1c).[19] Obviously, the cross-coupling reactions of 1,1-dibromoethylenes with organometal reagents is one of the most generally useful. However, this type of reactions has been less explored due to a complication of three competitive pathways (Scheme 1a–c). A key success of this



Scheme 1 The coupling reactions involving 1,1-dibromoethylenes **1** (a–d).

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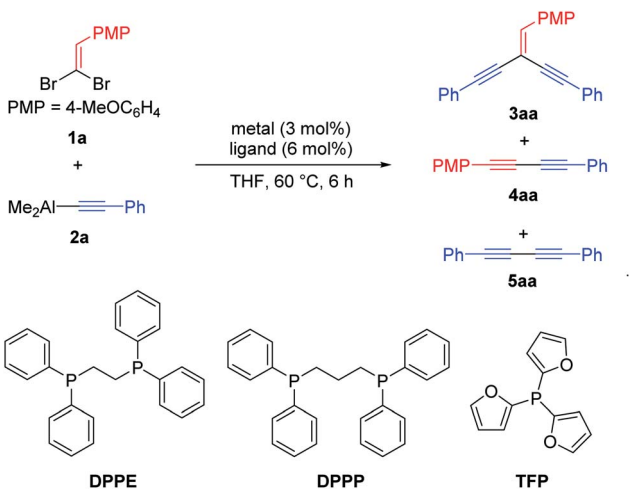
reaction relies mainly on suitable catalytic systems and/or appropriate organometallic reagents that can selectively produce either conjugated enediynes or 1,3-diynes.

To the best of our knowledge, the cross-coupling reaction of 1,1-dibromoethylenes with alkynylaluminums, which have been extensively used in organic synthesis,[20] has not been achieved. Herein, we would like to describe the novel Pd–phosphine complexes catalyzed selective cross-coupling reactions of 1,1-dibromoethylenes **1** with alkynylaluminums **2** to provide the aryl substituted conjugated enediynes **3** and unsymmetrical 1,3-diynes **4**, respectively (Scheme 1d).

Results and discussion

In the initial study, dimethyl(phenylethynyl)aluminum **2a** and 1,1-dibromoethylene **1a** were chosen as the model substrates for the synthesis of aryl substituted conjugated enediynes *via* cross-coupling reaction.[21] Various palladium salts were surveyed in THF at 60 °C and $PdCl_2$, $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$ could afford **3aa** in lower yield, meanwhile, the homo-coupling byproduct 1,4-diphenylbuta-1,3-diyne **5aa** was observed (Table 1, entries 1–3). When the reaction was performed with $Pd(OAc)_2$, an acceptable yield of **3aa** (36%) was obtained, and also the homo-coupling byproduct **5aa** was isolated in 16% yield (Table 1, entry 4). Unexpectedly, the cross-coupling product 1,3-diyne **4aa** as the major compound was achieved in 13% yield under $Pd_2(dba)_3$ catalysis (Table 1, entry 5). Further optimization of the reaction conditions was then aimed at exploring the efficiency of $Pd(OAc)_2$ with various P-ligands. Among them, the diphosphine ligands benefited the reactivity (Table 1, entries 6–9). As for the backbone moiety, the 1,2-bis(diphenylphosphanyl) ethane (DPPE) exhibited a slight superiority in reactivity toward this cross-coupling compared with 1,3-bis(diphenylphosphanyl) propane (DPPP) (Table 1, entry 8 *vs.* 9). To further improve the conversion, the efficiency of additives was then examined (Table 1, entries 10–12). We were delighted to find that the addition of 10 mol% of K_3PO_4 as additive could improve the yield of **3aa** to 80% and only trace of byproducts **4aa** and **5aa** were observed (Table 1, entry 11). Therefore, the optimal conditions were identified as 3 mol% of $Pd(OAc)_2$ with 6 mol% of DPPE, 10 mol% of K_3PO_4 as additive in THF at 60 °C for 6 h.

Table 1 Optimization of the reaction conditions for the synthesis of conjugated enediynes[a]



Entry	Metal/ligand/base	Yield[b] (%) 3aa	4aa	5aa
1	$PdCl_2$	17	Trace	22
2	$Pd(PPh_3)_2Cl_2$	15	Trace	26
3	$Pd(PPh_3)_4$	14	Trace	24
4	$Pd(OAc)_2$	36	Trace	16
5	$Pd_2(dba)_3$	Trace	13	Trace
6	$Pd(OAc)_2/PPh_3$	56	Trace	7
7	$Pd(OAc)_2/PCy_3$	45	Trace	5
8	$Pd(OAc)_2$/DPPE	70	Trace	Trace
9	$Pd(OAc)_2$/DPPP	55	Trace	10
10	$Pd(OAc)_2/DPPE/Cs_2CO_3$	32	Trace	Trace
11	$Pd(OAc)_2/DPPE/K_3PO_4$	80	Trace	Trace
12	$Pd(OAc)_2/DPPE/Et_3N$	75	Trace	Trace

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), metal (3 mol%), ligand (6 mol%), base (10 mol%), THF (1.0 mL), 60 °C, 6 h, under Ar. [b] Isolated yield.

Under the optimal conditions (Table 1, entry 11), various 1,1-dibromoethylenes **1** and alkynylaluminum reagents **2** were evaluated, affording the corresponding aryl substituted conjugated enediynes **3** with moderate to good yields (up to 93%) and the trace of 1,3-diyne byproducts **4** and **5** were not isolated. As shown in Table 2, the reactivity of the cross-coupling was sensitive to the steric hindrance rather than to the electronic property of substituents on the phenyl ring of 1,1-dibromoethylenes **1**. The substrates **1** with *ortho*-substituents gave lower yields than those with *para* ones (Table 2, entries 2 *vs.* 1, 6 *vs.* 5 and 8 *vs.* 7). Meanwhile, the fused-ring and heteroaromatic substrates (**1m**, **1n** and **1o**) were also tolerable, giving the desired products with 51% to 93% yields (Table 2, entries 11, 12, 13, 16, 19, 20, 24 and 28). On the other hand, the reactivity of this reaction was sensitive to neither the electronic properties nor the steric hindrance of substituents on the phenyl ring of alkynylaluminums **2**. Generally, the desired conjugated enediynes **3** were isolated with good to excellent yields (up to 93%) except **3fa** and **3oa** (53% and 51% yields, Table 2, entries 6 and 13). Moreover, the 2-thienyl substituted substrate **2g** also successfully afforded the desired products with good yields (Table 2, entries 26–28).[22]

Inspired by the previous discovery (Table 1, entry 5), it was envisioned that the aryl substituted unsymmetrical 1,3-diynes **4** could be achieved *via* cross-coupling reaction of 1,1-dibromoethylenes **1** with alkynylaluminums **2** in the presence of $Pd_2(dba)_3$. Thus, we then restarted to optimize the reaction conditions of this $Pd_2(dba)_3$ catalyzed cross-coupling using **1a**[21] and **2a** as the model substrates, respectively, in which the conjugated enediyne **3aa** and homo-coupling byproduct 1,4-diphenylbuta-1,3-diyne **5aa** were not determined. Performing the reaction in THF at higher temperature afforded the desired product **4aa** with higher yield [Table 3, entries 2 (80 °C) *vs.* 1 (60 °C)]. To improve the reactivity, the efficiency of solvent was then examined and it was found that the polar aprotic solvents were

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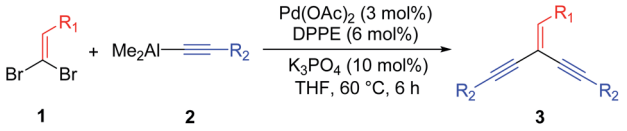
Table 2 Substrate scope for the synthesis of conjugated enediynes[a]



1 2 3

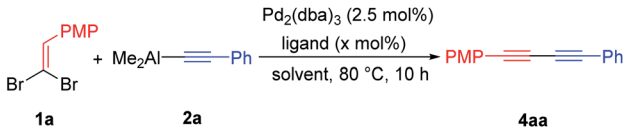
Entry	R_1	R_2	3	Yield[b] (%)
1	4-$MeOC_6H_4$	Ph	**3aa**	80
2	2-$MeOC_6H_4$	Ph	**3ba**	61
3	4-MeC_6H_4	Ph	**3ca**	83
4	3-MeC_6H_4	Ph	**3da**	91
5	4-FC_6H_4	Ph	**3ea**	72
6	2-FC_6H_4	Ph	**3fa**	53
7	4-ClC_6H_4	Ph	**3ga**	83
8	2,4-$Cl_2C_6H_3$	Ph	**3ha**	76
9	4-BrC_6H_4	Ph	**3ja**	75
10	4-$F_3CC_6H_4$	Ph	**3la**	71
11	1-Naphthyl	Ph	**3ma**	66
12	2-Thienyl	Ph	**3na**	69
13	2-Furyl	Ph	**3oa**	51
14	4-$MeOC_6H_4$	4-MeC_6H_4	**3ab**	77
15	4-BrC_6H_4	4-MeC_6H_4	**3jb**	88
16	1-Naphthyl	4-MeC_6H_4	**3mb**	74
17	4-$MeOC_6H_4$	3-MeC_6H_4	**3ac**	75
18	3-BrC_6H_4	3-MeC_6H_4	**3kc**	89
19	1-Naphthyl	3-MeC_6H_4	**3mc**	93
20	2-Thienyl	3-MeC_6H_4	**3nc**	69
21	4-MeC_6H_4	4-FC_6H_4	**3cd**	72
22	4-BrC_6H_4	4-FC_6H_4	**3jd**	89
23	3-BrC_6H_4	4-FC_6H_4	**3kd**	84
24	2-Thienyl	4-FC_6H_4	**3nd**	83
25	4-BrC_6H_4	3-FC_6H_4	**3je**	66
26	4-$MeOC_6H_4$	2-Thienyl	**3ag**	65
27	4-MeC_6H_4	2-Thienyl	**3cg**	70
28	2-Thienyl	2-Thienyl	**3ng**	71

[a] Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), $Pd(OAc)_2$ (3 mol%), DPPE (6 mol%), K_3PO_4 (10 mol%), THF (1.0 mL), 60 °C, 6 h, under Ar. [b] Isolated yield.

beneficial (Table 3, entries 3 and 4). Further optimization of the reaction conditions was then aimed at exploring the efficiency of $Pd_2(dba)_3$ with various P-ligands. The addition of DPPE, which had been proved to be the most effective ligand in the synthesis of conjugated enediyne **3aa**, could hardly provide the target product **4aa** (Table 3, entry 5). Delightedly, when the reaction was carried out with 5.0 mol% of tri(2-furyl)phosphine (TFP, Table 1) as ligand, the desired 1,3-diyne **4aa** could be isolated in 45% yield (Table 3, entry 8). Increasing the amount of TFP to 15.0 mol% could greatly improve the yield to 60% (Table 3, entry 9). The addition of 1.5 equiv. of diisopropyl ethylamine (DIPEA) could further enhance the yield to 74% (Table 3, entry 10). Thence, the optimal conditions were identified as 2.5 mol% of $Pd_2(dba)_3$ with 15.0 mol% of TFP, 1.5 equiv. of DIPEA in DMF at 80 °C for 10 h.

With the optimal reaction conditions in hand (Table 3, entry 10), the substrate scope of 1,1-dibromoethylenes **1** with alkynylaluminums **2** was next examined and also the conjugated enediynes **3** and homo-coupling byproducts 1,3-diynes **5** were

Table 3 Optimization of the reaction conditions for the synthesis of unsymmetrical 1,3-diynes[a]

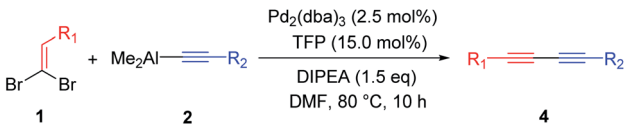


1a 2a 4aa

Entry	Ligand	x (mol%)	Solvent	Yield[b] (%)
1[c]	—	5	THF	12
2	—	5	THF	18
3	—	5	DMSO	26
4	—	5	DMF	28
5	DPPE	5	DMF	Trace
6	PPh_3	5	DMF	19
7	PCy_3	5	DMF	21
8	TFP	5	DMF	45
9	TFP	15	DMF	60
10[d]	TFP	15	DMF	74

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.8 mmol), $Pd_2(dba)_3$ (2.5 mol%), ligand (x mol%), solvent (3.0 mL), 80 °C, 10 h, under Ar. [b] Isolated yield. [c] Reaction was performed at 60 °C. [d] DIPEA (0.75 mmol) was added as additive.

Table 4 Substrate scope for the synthesis of unsymmetrical 1,3-diynes[a]



1 2 4

Entry	R_1	R_2	4	Yield[b] (%)
1	4-$MeOC_6H_4$	Ph	**4aa**	74
2	4-MeC_6H_4	Ph	**4ca**	97
3	3-MeC_6H_4	Ph	**4da**	78
4	2-FC_6H_4	Ph	**4fa**	82
5	2-ClC_6H_4	Ph	**4ia**	78
6	1-Naphthyl	Ph	**4ma**	69
7	4-MeC_6H_4	4-MeC_6H_4	**4cb**	68
8	3-MeC_6H_4	4-MeC_6H_4	**4db** (**4cc**)	99
9	4-FC_6H_4	4-MeC_6H_4	**4eb** (**4cd**)	91
10	2-FC_6H_4	4-MeC_6H_4	**4fb**	81
11	1-Naphthyl	4-MeC_6H_4	**4mb**	66
12	2-Furyl	4-MeC_6H_4	**4ob**	59
13	4-MeC_6H_4	3-MeC_6H_4	**4cc** (**4db**)	74
14	3-MeC_6H_4	3-MeC_6H_4	**4dc**	89
15	2-FC_6H_4	3-MeC_6H_4	**4fc** (**4df**)	77
16	2-Furyl	3-MeC_6H_4	**4oc**	61
17	4-MeC_6H_4	4-FC_6H_4	**4cd** (**4eb**)	64
18	3-MeC_6H_4	4-FC_6H_4	**4dd**	69
19	3-MeC_6H_4	2-FC_6H_4	**4df** (**4fc**)	70
20	2-FC_6H_4	2-FC_6H_4	**4ff**	63
21	4-MeC_6H_4	2-Thienyl	**4cg**	61

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.8 mmol), $Pd_2(dba)_3$ (2.5 mol%), TFP (15.0 mol%), DIPEA (0.75 mmol), DMF (3.0 mL), 80 °C, 10 h, under Ar. [b] Isolated yield.

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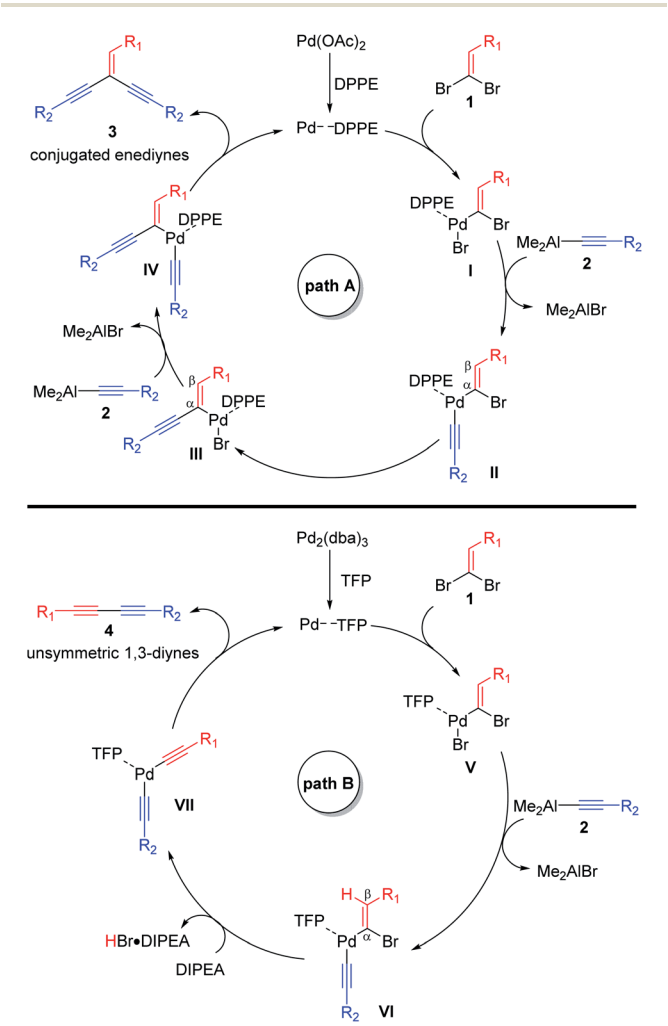
not determined. As shown in Table 4, the electronic or positional nature of the substituents either in 1,1-dibromoethylenes **1** or in alkynylaluminums **2** had nearly no effect on the efficiency of this cross-coupling reaction, affording the aryl substituted unsymmetrical 1,3-diynes **4** with good to excellent yields (up to 99%). For the fused-ring substrate **1m**, the expected products **4ma** and **4mb** were obtained in good yields (Table 4, entries 6 and 11). Especially, the 2-thienyl or 2-furyl substituted substrates successfully afforded the unsymmetrical 1,3-diynes **4ob**, **4oc** and **4cg** in good yields (Table 4, entries 12, 16 and 21).[22]

According to the previous studies on the palladium catalyzed cross-coupling reactions[11–13] and our previous works about organoaluminums,[20g–l] two reasonable catalytic cycles are proposed in Scheme 2. The possible mechanism of the cross-coupling for producing enediynes **3** is shown in path A. First, the oxidative additions of 1,1-dibromoethylenes **1** to Pd–DPPE complex generate the organopalladium(II) bromide intermediates **I**. Then, the transmetalations of alkynylaluminums **2** with intermediates **I** give complex intermediates **II** and Me_2AlBr. The intermediates **II** with another alkenyl bromide could isomerize into complex intermediates **III** *via* intramolecular Pd^{II}-translation. Next, the transmetalation of alkynylaluminums **2** with intermediates **III** provided complex intermediates **IV** and another Me_2AlBr again. Finally, intermediates **IV** under goes reductive eliminations to afford the desired aryl substituted conjugated enediynes **3** and regenerate the active Pd–DPPE species for the next catalytic cycle. Similar to path A, the possible mechanism of the cross-coupling for producing unsymmetrical 1,3-diynes **4** is shown in path B. Oxidative additions of 1,1-dibromoethylenes **1** to Pd–TFP generate the organopalladium(II) bromide intermediates **V** and transmetalations of alkynylaluminums **2** with intermediates **V** give intermediates **VI** and Me_2AlBr. Elimination of the β-H in intermediates **VI**, in which the acidities of β-H of intermediates **VI** could probably be stronger than those of intermediates **II** so that this elimination could be promoted by an equiv. amount of DIPEA, generate intermediates **VII** and HBr·DIPEA. Finally, intermediates **VII** also under goes reductive eliminations to afford the desired aryl substituted unsymmetrical 1,3-diynes **4** and regenerate the active Pd–TFP species for the next catalytic cycle.



Scheme 2 Proposed catalytic cycles.

Conclusions

Though the specific mechanism and reason why the same starting materials could selectively produce either conjugated enediynes or unsymmetrical 1,3-diynes in analogous Pd–phosphine catalytic system were unclear, we have successfully developed a highly efficient method for the synthesis of aryl substituted conjugated enediynes and unsymmetrical 1,3-diynes *via* selective cross-coupling reactions of 1,1-dibromoethylenes with alkynylaluminums using $Pd(OAc)_2$–DPPE and $Pd_2(dba)_3$–TFP complexes as catalysts, respectively. A series of aryl substituted conjugated enediynes **3** and unsymmetrical 1,3-diynes **4** have been obtained in moderate to excellent yields (up to 99%). To the best of our knowledge, there is no precedent for the application of 1,1-dibromoethylenes and alkynylaluminums in cross-coupling reaction to date. Further mechanistic studies of these selective cross-coupling reactions are still in progress.

Conflicts of interest

There are no conflicts to declare.

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21 The *p*-methoxyphenyl substituted 1,1-dibromoethylene **1a** was selected as the model substrate to facilitate purification and distinguish from the homo-coupling product.

22 Under the optimal reaction conditions, no products were observed for alkyl or cycloalkyl substituted alkynylaluminums.

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