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Iridium-Catalyzed Allylic Alkylations of Sodium Phenyl Selenide

Cui, Ruimin[a](崔瑞敏) Guo, Xinwen[b](郭新闻)
Zheng, Shengcai[a](郑生财) Zhao, Xiaoming*,[a](赵晓明)

[a] *Department of Chemistry, Tongji University, Shanghai 200092, China*
[b] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, Liaoning 116012, China*

An iridium-catalyzed allylic substitution of sodium phenyl selenide with unsymmetrical allyl carbonates was accomplished, which produced the linear allyl phenyl selenides in 38%—74% yields. An asymmetric iridium-catalyzed allylation of sodium phenyl selenide was presented as well.

Keywords sodium phenyl selenide, allylation, iridium, phosphoramidite ligand, allyl phenyl selenide

Introduction

Iridium-catalyzed allylic substitution has become one of the powerful methods for the formation of carbon-carbon[1] and carbon-heteroatom bond (*e.g.*, carbon-nitrogen,[2] carbon-oxygen,[3] and carbon-sulfur[4]). To date, carbon-selenium bond construction by means of iridium-catalyzed allylation reaction is not explored yet. Likewise, transition metals such as palladium[5] and ruthenium[6] have already been used as a catalyst in the allylation reaction. In general, oxidative addition of the allylic substrate to a low-valent iridium complex forms a π-allyl complex, which tends to lead to preferential attack of nucleophile at the more substituted allylic terminus to produce the branched allylic products.[7] Allyl selenides, which are versatile intermediates in organic synthesis,[8] may undergo [2,3]-sigmatropic rearrangement under various conditions to form allyl amines,[9] halides,[10] and alcohols.[11] Moreover, organoselenium compounds possess important potential as anticancer and antioxidant agents.[12] In connection of our study on carbon-sulfur bond formation catalyzed via iridium complex,[4d-4g] we subsequently investigate iridium-catalyzed allylic alkylation using sodium phenyl selenide as a nucleophile. In this paper, we report iridium-catalyzed allylic substitution of sodium phenyl selenide with a range of methyl allyl carbonates, which produce the linear allyl phenyl selenides in good yields. The asymmetric iridium-catalyzed allylations of sodium phenyl selenide were discussed as well.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded using Bruker AM-400 spectrometer in $CDCl_3$ with TMS as an internal standard. Melting points were recorded using a WRS-2A micro melting point apparatus and were uncorrected. ^{19}F NMR spectra were obtained at 282 MHz, and CF_3CO_2H was used as an internal standard. A Nicolet AVATAR 360 FT-IR spectrophotometer was used for IR spectra. HPLC analyses were carried out on chiral columns (Daicel CHIRALCEL OJ-H) with a Shimadzu 150 instrument fitted with a multi-wavelength detector. Low-resolution electron-impact (EI) mass spectra were obtained with an Agilent MSD Chemstation, and high-resolution mass spectra were obtained with a Finnigan VG Platform or a Finnigan MAT 95S. Commercially obtained reagents were used without further purification. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

Synthesis of compound 3

$[Ir(COD)Cl]_2$ (0.0060 mmol, 3.0 mol%), [*O*,*O*'-(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N*,*N*'-di-(*S*,*S*)-[phenylethyl-phosphoramidite] (**L1,** 0.0012 mmol, 6.0 mol%), THF (0.5 mL), and propylamine (0.2 mL) were placed in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 ℃ for 30 min and then the volatile

* E-mail: xmzhao08@mail.tongji.edu.cn; Tel.: 0086-21-65981376; Fax: 0086-21-65981376
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solvents were removed under vacuum to give a yellow solid. After that, allyl carbonate **2** (0.24 mmol, 120 mol%), sodium phenyl selenide **1** (0.20 mmol), and DCE (2.0 mL) were added. The reaction mixture was stirred at room temperature until the mixture became clear. Then the crude reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The ratio of regioisomers (branched to linear) was determined by ^{1}H NMR of the crude reaction mixture or the mixture of these two compounds. The crude residue was purified by flash column chromatography (petroleum ether/dichloromethane) to give the desired products.

The phosphoramidite ligands,[13] substituted allyl carbonates,[14] and sodium phenyl selenide[15] were prepared according to known procedures.

(*E*)-Cinnamyl(phenyl)selane (3a)[16] White solid, m.p. 64.3—65.1 ℃, yield: 40.5 mg (72%). ^{1}H NMR spectroscopy showed a 99∶1 linear∶branched ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53—7.51 (m, 2H), 7.28—7.18 (m, 8 H), 6.33 (dt, J=15.6, 7.6 Hz, 1H), 6.23 (d, J=15.6 Hz, 1H), 3.69 (d, J=7.6 Hz, 2H).

(*E*)-(3-(4-Methoxyphenyl)allyl)(phenyl)selane (3b)[17] White solid, m.p. 89.7—91.0 ℃, yield: 34.1 mg (56%). ^{1}H NMR spectroscopy showed a 99∶1 linear∶branched ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53—7.51 (m, 2H), 7.26—7.20 (m, 5H), 6.82 (d, J=8.8 Hz, 2H), 6.23—6.13 (m, 2H), 3.79 (s, 3H), 3.67 (d, J=6.4 Hz, 2H).

(*E*)-(3-(4-Chlorophenyl)allyl)(phenyl)selane (3c)[17] Lemon yellow solid, m.p. 72.7—73.5 ℃, yield: 31.4 mg (51%). ^{1}H NMR spectroscopy showed a 99∶1 linear∶branched ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52—7.50 (m, 2H), 7.26—7.23 (m, 5H), 7.18 (d, J=8.8 Hz, 2H), 6.28 (dt, J=15.6, 7.6 Hz, 1H), 6.15 (d, J=15.6 Hz, 1H), 3.66 (d, J=7.6 Hz, 2H).

(*E*)-Phenyl(3-*p*-tolylallyl)selane (3d)[6] White solid, m.p. 67.0—68.2 ℃, yield: 39.2 mg (68%). ^{1}H NMR spectroscopy showed a 99∶1 linear∶branched ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52—7.50 (m, 2H), 7.24—7.22 (m, 3H), 7.16 (d, J=8 Hz, 2H), 7.07 (d, J=8 Hz, 2H), 6.27 (dt, J=15.6, 7.2 Hz, 1H), 6.20 (d, J=15.6 Hz, 1H), 3.66 (d, J=6.8 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2, 134.0, 133.9, 132.0, 130.0, 129.1, 128.9, 127.2, 126.1, 124.8, 30.8, 21.1; IR (KBr) v: 3428, 2917, 2362, 1645, 1629, 1565, 1503, 1469, 1263, 1021, 757, 699, 662 cm^{-1}. MS (EI) m/z: 288 (M^+). HRMS (EI) calcd for $C_{16}H_{16}Se$ (M^+): 288.0417, found 288.0414.

(*E*)-(3-(3-Methoxyphenyl)allyl)(phenyl)selane (3e) Yellow oil, yield: 39.5 mg (65%). ^{1}H NMR spectroscopy showed a 99∶1 linear∶branched ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53—7.51 (m, 2H), 7.26—7.25 (m, 3H), 7.19 (t, J=8.0 Hz, 1H), 6.87 (d, J=7.6 Hz, 1H), 6.81 (s, 1H), 6.76 (d, J=8 Hz, 1H), 6.32 (dt, J=15.6, 7.6 Hz, 1H), 6.20 (d, J=15.6 Hz, 1H), 3.80 (s, 3H), 3.68 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 138.3, 134.0, 132, 129.4, 129.0, 127.4, 126.2, 119.0, 113.1, 111.6, 91.7, 55.2, 30.6; IR (KBr) v: 3054, 2934, 2841, 1645, 1566, 1430, 1263, 1147, 971, 702, 659 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{16}OSe$ (M^+): 304.0366, found 304.0367.

(*E*)-Phenyl(3-(3-(trifluoromethyl)phenyl)allyl)selane (3f) White solid, m.p. 54.8—55.8 ℃, yield: 49.9 mg (73%). ^{1}H NMR spectroscopy showed a 99∶1 linear∶branched ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53—7.51 (m, 2H), 7.48 (s, 1H) 7.46—7.38 (m, 3H), 7.27—7.26 (m, 3H), 6.39 (dt, J=15.6, 7.6 Hz, 1H), 6.20 (d, J=15.6 Hz, 1H), 3.68 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.6, 134.2, 130.9 (q, J=31.9 Hz), 130.5, 129.5, 129.3, 129.0, 128.9, 128.0, 127.6, 124.1 (q, J=270.7 Hz), 123.9 (q, J=3.8 Hz), 122.9 (q, J=3.8 Hz), 30.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.63 (s); IR (KBr) v: 3050, 2941, 1579, 1476, 1449, 1333, 1300, 1180, 1127, 1064, 991, 951, 891, 791, 745, 729, 705, 685, 662 cm^{-1}. MS (EI) m/z: 342 (M^+). HRMS (EI) calcd for $C_{16}H_{13}F_3Se$ (M^+): 342.0135, found 342.0138.

(*E*)-2-(3-(Phenylselanyl)prop-1-enyl)thiophene (3g) White solid, m.p. 56.7—57.4 ℃, yield: 21.3 mg (38%). ^{1}H NMR spectroscopy showed a 99∶1 linear∶branched ratio. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53—7.51 (m, 2H), 7.27—7.25 (m, 3H), 7.11 (d, J=5.2 Hz, 1H), 6.92 (dd, J=7.6, 7.6 Hz, 1H), 6.84 (d, J=3.2 Hz, 1H), 6.36 (d, J=15.6 Hz, 1H), 6.16 (dt, J=15.6, 7.6 Hz, 1H), 3.56 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.8, 134.0, 129.7, 129.0, 127.4, 127.3, 125.6, 125.3, 125.2, 124.0, 30.5; IR (KBr) v: 3468, 2353, 1696, 1679,1636, 1632, 1257, 950, 725, 696 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{12}SSe$ (M^+): 279.9825, found 279.9853.

(*E*)-Phenyl(5-phenylpent-2-enyl)selane (3h)[18] Yellow oil, yield: 40.4 mg (67%). ^{1}H NMR spectroscopy showed a 99∶1 linear∶branched ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49—7.46 (m, 2H), 7.28—7.24 (m, 5H), 7.17 (t, J=7.2 Hz, 1H), 7.10 (d, J=7.2 Hz, 2H), 5.60 (dt, J=15.2, 7.2 Hz, 1H), 5.42 (dt, J=15.2, 6.4 Hz, 1H), 3.48 (d, J=7.6 Hz, 2H), 2.56 (t, J=7.6 Hz, 2H), 2.27 (dt, J=8.0, 7.2 Hz, 2H).

(*E*)-Hex-2-enyl(phenyl)selane (3i)[19] Yellow oil, yield: 25.9 mg (54%). ^{1}H NMR spectroscopy showed a 89∶11 linear∶branched ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53—7.47 (m, 2H), 7.25—7.24 (m, 3H), 6.56 (dt, J=15.2, 7.6 Hz, 1H), 5.39 (dt, J=15.2, 6.8 Hz, 1H), 3.50 (d, J=7.2 Hz, 2H), 1.93 (dt, J=7.2, 7.2 Hz, 2H), 1.33—1.24 (m, 2H), 0.82 (t, J=7.2 Hz, 3H).

Synthesis of compounds 5

$[Ir(COD)Cl]_2$ (0.0060 mmol, 3.0 mol%), [*O*,*O*'-(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N*,*N*'-di-(*S*,*S*)-[phenylethyl-phosphoramidite] (**L1**, 0.0012 mmol, 6.0 mol%), THF (0.5 mL), and propylamine (0.2 mL) were placed in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 ℃ for 30 min and then the volatile solvents were removed under vacuum to give a yellow solid. After that, allyl carbonate **2** (0.24 mmol, 120

mol%), sodium phenyl selenide **1** (0.20 mmol), and DCE (2.0 mL) were added. The reaction mixture was stirred at room temperature for 1 h, and then the solvent was removed under vacuum. After 1 h, NBSH (0.48 mmol, 240 mol%), Et_3N (0.96 mmol, 480 mol%), THF (2.0 mL) and *i*-PrOH (2.0 mL) were added at 30 ℃. The reaction was carried our overnight.[4g] Then the crude reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (petroleum ether/dichloromethane) to give the desired products and the ratio of regioisomers (branched to linear).

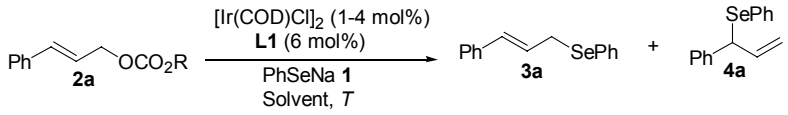
Phenyl(1-phenylpropyl)selane (5a)[20] Yellow oil, yield: 18.7 mg (34%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40—7.38 (m, 2H), 7.16—7.26 (m, 8H), 4.15 (t, J=7.6 Hz, 1H), 2.06 (q, J=7.6 Hz, 2H), 0.90 (t, J=7.6 Hz, 3H). The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 ℃) {t_R=14.96 min (minor); 8.64 min (major) [Daicel CHIRALCEL OJ-H (0.46 cm×25 cm), hexane/2-propanol, 90/10, 1 mL/min]} to be 90%. $[\alpha]_D^{20}$ =−41.6 (*c* 0.3, $CHCl_3$).

Phenyl(1-phenylpentan-3-yl)selane (5h) Yellow oil，yield: 18.8 mg (31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54—7.51 (m, 2H), 7.28—7.25 (m, 5H), 7.20—7.14 (m, 3H), 3.10 (q, J=6.4 Hz, 1H), 2.82—2.75 (m, 2H), 1.97—1.90 (m, 2H), 1.74—1.67 (m, 2H), 1.02 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.8, 134.9, 129.3, 128.9, 128.5, 128.3, 127.3, 125.8, 47.8, 36.6, 33.9, 28.3, 12.1; IR (KBr) ν: 3430.09, 2918, 2851, 1662, 1586, 1383, 1236, 853, 715. HRMS (EI) calcd for $C_{17}H_{20}Se$ (M^+): 298.0790, found 298.0791. The enantiomeric excess of the product was determined by HPLC analysis (214 nm, 25 ℃) {t_R=5.30 min (minor); 5.87 min (major) [Daicel CHIRALCEL OJ-H (0.46 cm×25 cm), hexane/2-propanol, 90/10, 1 mL/min]} to be 94%. $[\alpha]_D^{20}$ +49.1 (*c* 0.4, $CHCl_3$).

Results and Discussion

We first carried out a reaction between sodium phenyl selenide (PhSeNa, **1**) and (*E*)-cinnamyl methyl carbonate **2a** in the presence of a well-known iridacycle[2b] (generated from 3 mol% of $[Ir(COD)Cl]_2$ and 6 mol% of chiral phosphoramidite ligand **L1**) in order to explore the asymmetric allylation. Unexpectedly, initial probing in 1,2-dichloroethene (DCE) at room temperature indicated that the linear allyl phenyl selenide **3a** as the major product instead of the branched allyl phenyl selenide **4a** was achieved in 53% yield (Table 1, Entry 1), which is not in agreement with the results obtained by iridium-catalyzed allylation of sodium thiophenoxide (PhSNa).[4d] Monitoring this reaction by ^{1}H NMR revealed that there appeared peaks at δ 5.0 (dd, J=10 Hz) during the process of the reaction, which were distributed into the corresponding terminus double bond of **4a**.[21] These results suggested that **4a**, which was first formed and could not be stopped at this stage, was further converted into **3a**. Taking into the consideration of the importance of the linear allyl phenyl selenide **3** in synthetic chemistry,[8] we consequently turned our attention to study on the synthesis of the linear allyl phenyl selenide **3**. The influence of solvents on this reaction was investigated. DCE was the optimum

Table 1 Optimization of iridium-catalyzed allylic substitution of sodium benzeneselenolate **1** with (*E*)-cinnamyl carbonate **2a**[a]



Entry	$[Ir(COD)Cl]_2$ (mol%)	Temp./℃	Sol.	R	**1**/**2a**	**3a**/**4a**[b]	Yield of **3a**[c]/%
1	3	25	DCE	Me	1/1.2	99/1	53
2	3	25	DCM	Me	1/1.2	98/2	50
3	3	25	THF	Me	1/1.2	99/1	28
4	3	25	PhMe	Me	1/1.2	99/1	32
5	3	25	DCE	Et	1/1.2	99/1	74
6	3	25	DCE	*t*-Bu	1/1.2	99/1	42
7	4	25	DCE	Et	1/1.2	99/1	62
8	2	25	DCE	Et	1/1.2	99/1	58
9	1	25	DCE	Et	1/1.2	99/1	51
10	3	0	DCE	Et	1/1.2	99/1	55
11	3	-10	DCE	Et	1/1.2	—[d]	—[d]
12	3	50	DCE	Et	1/1.2	99/1	26
13	3	25	DCE	Et	1/2	99/1	62
14	3	25	DCE	Et	2/1	99/1	54

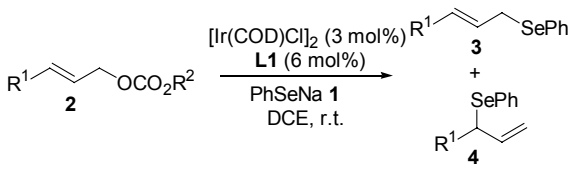
[a] Reaction conditions: 1—4 mol% of $[Ir(COD)Cl]_2$, 6 mol% of **L1**, 120 mol% of **2a**, and 100 mol% of PhSeNa **1** (0.1 mol/L). [b] Determined by ^{1}H NMR of the crude reaction mixture. [c] Isolated yield. [d] No desired product was observed in this case.

solvent and other solvents such as DCM, THF, and toluene gave poor yields (Table 1, Entries 2—4). The influence of the leaving groups including OCO_2Me, OCO_2Et, and OCO_2Bu-*t* on efficiency and selectivity was examined and we found that OCO_2Et led to the highest yield (74%, Table 1, Entries 1, 5 and 6).

Furthermore, change in the catalyst loading has a considerable effect on this reaction. 3 mol% of iridium complex gave rise to the highest yield of **3a** (Entries 5 and 7—9). The reaction was performed at a range of −10 to 50 ℃, among them, only room temperature gave the highest yield of **3a** (Entries 5 and 10—12). Subsequent optimization studies indicated that use of excess amounts of either PhSeNa **1** or allylic substrate **2a** led to somewhat reduction of the yield (Entries 5, 13 and 14).

Using the optimized conditions, the scope of a diversity of allyl carbonates **2** was further studied. As shown in Table 2, all aromatic allyl carbonates **2a**—**2f** with either electron-donating group (*e.g.*, 4-MeO, 4-CH_3, and 3-CH_3O) or electron-withdrawing group (*e.g.*, 4-Cl and 3-CF_3) on the phenyl ring gave the corresponding **4a**—**4f** in 51%—74% yields (Entries 1—6). 2-Thienyl allylic carbonate **2g** resulted in a slightly lower yield (38%, Entry 7). Aliphatic allyl carbonates **2h**—**2i** also worked well (Entries 8 and 9).

Table 2 Iridium-catalyzed allylic substitution of a diversity of allyl carbonates with **1**[a]

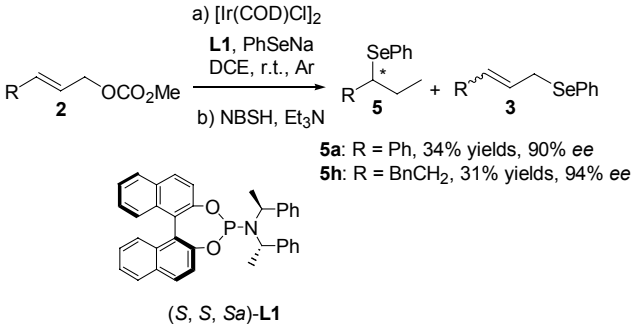


Entry	R^1	R^2	**3**/**4**[b]	Yield of **3**[c]/%
1	C_6H_5	Et	99/1	**3a**, 74
2	4-$MeOC_6H_4$	Et	99/1	**3b**, 56
3	4-ClC_6H_4	Me	99/1	**3c**, 51
4	4-MeC_6H_4	Et	99/1	**3d**, 68
5	3-$MeOC_6H_4$	Et	99/1	**3e**, 65
6	3-$CF_3C_6H_4$	Et	99/1	**3f**, 73
7	2-Thienyl	Me	99/1	**3g**, 38
8	$PhCH_2CH_2$	Et	99/1	**3h**, 67
9	$CH_3CH_2CH_2$	Me	89/11	**3i**, 54

[a] Reaction conditions: 3 mol% of $[Ir(COD)Cl]_2$, 6 mol% of **L1**, 120 mol% of **2**, and 100 mol% of **1** (0.2 mol/L) in DCE at 25 ℃. [b] Determined by ^1H NMR of the crude reaction mixture. [c] Isolated yields.

The enantioselective iridium-catalyzed allylic alkylation of PhSeNa **1** with methyl allyl carbonates **2** was also investigated and the representative examples were illustrated in Scheme 1. To avoid converting **4a** into **3a**, the allylation of PhSeNa **1** with (*E*)-cinnamyl methyl carbonate **2a** in the presence of an iridacycle[2b] was performed under the optimal conditions, followed by the reduction with *o*-nitrobenzenesfonylhyldrazide (NBSH), which is an effective reagent for the reduction of terminus alkenes.[22] The ethyl-substituted phenyl selenide **5a** was obtained in two steps in 34% yield with 90% *ee* along with the formation of **3a** (21% yield). Similarly, aliphatic substrate **2h** was used in this reaction to provide **5h** in two steps in 31% yields with 94% *ee* together with the formation of **3h** (22% yield).

Scheme 1 The asymmetric iridium-catalyzed allylation of sodium phenyl selenide



Conclusions

We have developed a practical method for the synthesis of the linear allyl phenyl selenides by iridium-catalyzed allylic substitution of sodium phenyl selenide **1** with a range of allyl carbonates **2**. The asymmetric iridium-catalyzed allylic alkylations of sodium phenyl selenide **1** were also explored, which gave the ethyl-substituted phenyl selenides **5** in two steps in 31%—34% yields with excellent enanioselectivities.

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