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Intramolecular Desulfitative Coupling: Nickel-Catalyzed Transformation of Diaryl Sulfones into Biaryls via Extrusion of SO_2

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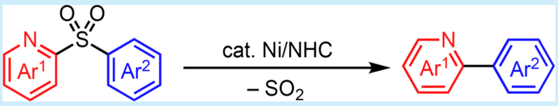
Supporting Information

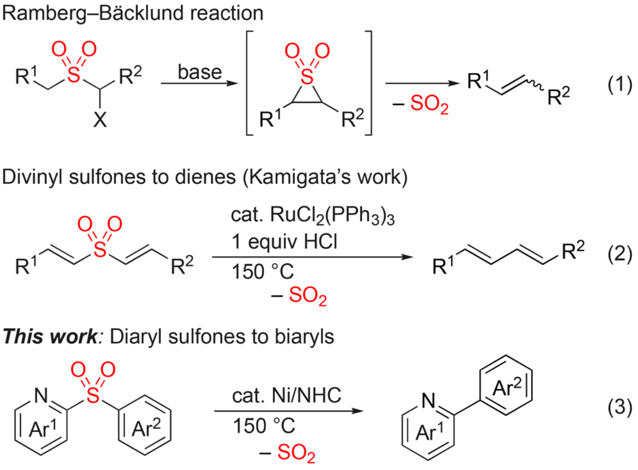
ABSTRACT: As a new transformation of organosulfur compounds, intramolecular desulfitative coupling of diaryl sulfones to the corresponding biaryls has been developed with the aid of nickel−NHC catalysts. This catalytic elimination of SO_2 was also applicable to alkenyl aryl sulfone to furnish the corresponding alkenyl arene.



Organosulfur compounds have occupied important positions not only as bioactive entities and functional materials but also as useful building blocks or reagents in organic synthesis.[1] Among organosulfur compounds, sulfones show intriguing reactivity owing to the low electron density and the good leaving ability of the sulfonyl unit.[1,2]

The Ramberg−Bäcklund reaction is a well-known reaction specific to dialkyl sulfones and has been extensively studied since its discovery in 1940.[3,4] The reaction mechanism includes intramolecular S_N2 reaction of α-haloalkyl sulfones followed by extrusion of SO_2 from episulfones to provide alkenes (Scheme 1, eq 1). This intramolecular process represents fascinating replacement of the SO_2 unit by a C−C double bond. Inspired by the elegant Ramberg−Bäcklund technology, we envisioned exploring a new intramolecular C−C bond-forming reaction with extrusion of SO_2. In particular, we focused our attention on intramolecular desulfitative coupling starting from unsaturated sulfones, considering the recent advances in catalytic C(sp^2)−S bond transformations.[5]

Scheme 1. Intramolecular Desulfitative Reactions



Arenesulfonylpalladiums or -rutheniums are known to expel SO_2 to form the corresponding arylmetal species. By virtue of this process, catalytic desulfitative couplings of arenesulfonyl chlorides, hydrazides, and sulfinate salts have been achieved. However, these reactions are limited to intermolecular coupling with external reagents.[6,7] To date, intramolecular desulfitative coupling of unsaturated sulfones has been limited to a ruthenium-catalyzed reaction reported by Kamigata (Scheme 1, eq 2).[8] However, this transformation only accommodates divinyl sulfones, and its synthetic utility remains unexplored. In light of the importance of biaryls in the chemical community, herein, we report intramolecular desulfitative coupling of diaryl sulfones into the corresponding biaryls by employing nickel−NHC (*N*-heterocyclic carbene) catalysts (Scheme 1, eq 3).[9,10]

By employing 2-naphthyl 2-quinolyl sulfone (**1a**) as a model substrate, we conducted optimization of the reaction conditions (Table 1). Owing to its potential for inert bond cleavage, we decided to use nickel catalysis.[11] After extensive screening of nickel precursors and ligands, a combination of $Ni(cod)_2$ and IMes generated *in situ* from IMes·HCl (Figure 1) and *t*-BuONa was found to be effective. In the presence of the catalyst, **1a** was heated in toluene under reflux (bath temp.: 150 °C). To facilitate departure of SO_2, a N_2 balloon was equipped to the reaction vessel. As a result, desired coupling product **2a** was obtained in 65% NMR yield (Table 1, entry 1). Small amounts of 2,2′-biquinolyl **3a** and 2,2′-binaphthyl **4a** were also obtained as byproducts. An addition of Mg turnings, which might reduce undesirably oxidized nickel species, improved the yield of **2a** to 74% (Table 1, entry 2). Coupling product **2a** was not obtained without either $Ni(cod)_2$ or IMes, whereas considerable amounts of **1a** were decomposed due to strongly basic *t*-BuONa and the high reaction temperature (Table 1, entries 3 and 4). The reaction in a closed vessel without a N_2 balloon decreased the yield of **2a**, while **1a** was almost consumed (Table 1, entry 5). Although other NHC ligands showed comparable reactivity, mono- and bidentate electron-rich phosphines such as PCy_3 and dcypt[12] did not work well (Table 1, entries 6−10).

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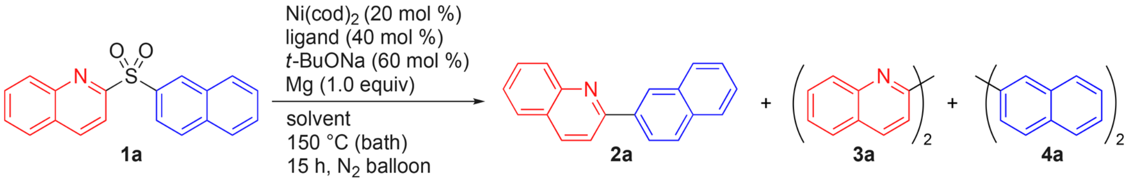
Table 1. Condition Screening



entry	ligand	solvent	conv of **1a** (%)[a]	yield of **2a** (%)[a]	yield of **3a** (%)[a,b]	yield of **4a** (%)[a,c]
1[d]	IMes·HCl	PhMe	93	65	6	14
2	IMes·HCl	PhMe	89	74	4	16
3[e]	IMes·HCl	PhMe	52	0	0	0
4	none	PhMe	50	0	24	2
5[f]	IMes·HCl	PhMe	94	56	2	18
6	IPr·HCl	PhMe	80	55	4	12
7	SIMes·HCl	PhMe	100	71	8	10
8	**L1**·HCl	PhMe	99	73	12	26
9[g]	PCy$_3$ (80 mol %)	PhMe	24	6	8	20
10[g]	dcypt	PhMe	1	0	0	0
11	IMes·HCl	1,4-dioxane	57	45	4	12
12	IMes·HCl	DMI	100	41	20	18
13	IMes·HCl	PhEt	63	42	8	14
14	IMes·HCl	mesitylene	59	33	6	10
15	IMes·HCl	PhMe/PhEt (v/v = 1/3)	100	80 (70[h])	4	18
16	**L1**·HCl	PhMe/PhEt (v/v = 1/3)	96	81 (71[h])	6	22
17[i]	**L1**·HCl	PhMe/PhEt (v/v = 1/3)	63	42	18	24
18[j]	**L1**·HCl	PhMe/PhEt (v/v = 1/3)	63	59	4	<10

[a] Determined by NMR. [b] Calculated based on the molar amount of the 2-quinolyl ring of **1a**. [c] Calculated based on the molar amount of the 2-naphthyl ring of **1a**. [d] Without Mg. [e] Without Ni(cod)$_2$. [f] Conducted in a closed tube. [g] Without *t*-BuONa. [h] Isolated yield. [i] With 20 mol % of ligand and 40 mol % of *t*-BuONa. [j] 5 mol % of Ni(cod)$_2$, 10 mol % of ligand, and 15 mol % of *t*-BuONa.

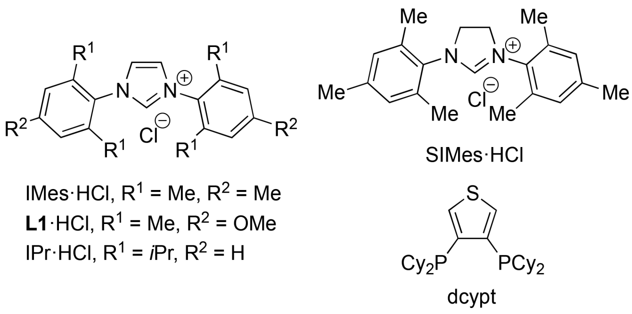


Figure 1. Ligands employed in Table 1. Cy = cyclohexyl.

We then investigated the solvent effect. The use of 1,4-dioxane instead of toluene lowered the conversion of **1a** (Table 1, entry 11). Significant amounts of byproducts **3a** and **4a** were formed when DMI was employed (Table 1, entry 12). Ethylbenzene and mesitylene having higher boiling points were not effective (Table 1, entries 13 and 14). We inferred that toluene acts not only as a simple solvent but also as a π-bonded ligand that would prevent undesired aggregation of catalytically active nickel species. Speculating that the bulkier ethyl group in ethylbenzene and the three methyl groups in mesitylene hampered its π-coordination to the nickel, we envisioned that a toluene/ethylbenzene cosolvent system would achieve a good balance between a higher reaction temperature and effective π-coordination. As we expected, the yield of **2a** was improved when the reaction was conducted in toluene/ethylbenzene (v/v = 1/3), and **2a** was isolated in 70% yield (Table 1, entry 15). Under the cosolvent conditions, the use of **L1**[13] was also effective to lead to isolation of **2a** in 71% yield (Table 1, entry 16). The reaction with 20 mol % of **L1** decreased the conversion of **1a** (Table 1, entry 17), which indicates a 2-fold amount, 40 mol %, of **L1** would suppress deactivating aggregation of nickel species that are generated through dissociation of **L1** at the high temperature. Notably, a 59% yield of **2a** was obtained even with 5 mol % of the nickel catalyst (Table 1, entry 18).

Having optimized the reaction conditions (Table 1, entry 16), we explored the scope of aryl 2-quinolyl sulfones (Scheme 2, a). Aryl sulfones bearing an electron-donating or -withdrawing group successfully reacted to afford the desired coupling products **2b**−**2h**. It is noteworthy that cyano and ester groups in **2g** and **2h** were tolerated during the reactions. 2-Methoxyphenyl sulfone **1i** gave coupling product **2i** in only 21% yield, probably due to the steric hindrance. Other aryl sulfones such as 1-naphthyl and 2-thienyl sulfones **1j** and **1k** were also applicable to the intramolecular coupling.

We then investigated the scope of azaaryl 2-naphthyl sulfones (Scheme 2, b). The intramolecular coupling reactions of 1-isoquinolyl sulfones **1l** and **1m** successfully occurred under the standard conditions to form biaryls **2l** and **2m** in 80% and 65% yields, respectively. The present catalysis was operative on a gram scale: 1.5 g (5.7 mmol, 71%) of **2l** was obtained from 8 mmol of **1l**. 2-Quinoxalyl, 2-pyrazyl, and 2-pyridyl sulfones **1n**−**p** were converted to biaryls **2n**−**p** albeit in moderate yields. The position of the C−SO$_2$ bond on the quinoline ring is important; 3-quinolyl and 4-quinolyl sulfones **1q** and **1r** resisted the reaction and were mostly recovered.

In our system, 2-azaaryl groups are necessary for catalytic turnover. Treatment of di(2-naphthyl) sulfone (**5**) under the catalytic conditions afforded **4a** in only 18% yield (Scheme 3). By means of a stoichiometric amount of the Ni−IMes complex, the yield of **4a** could be increased to 50%.

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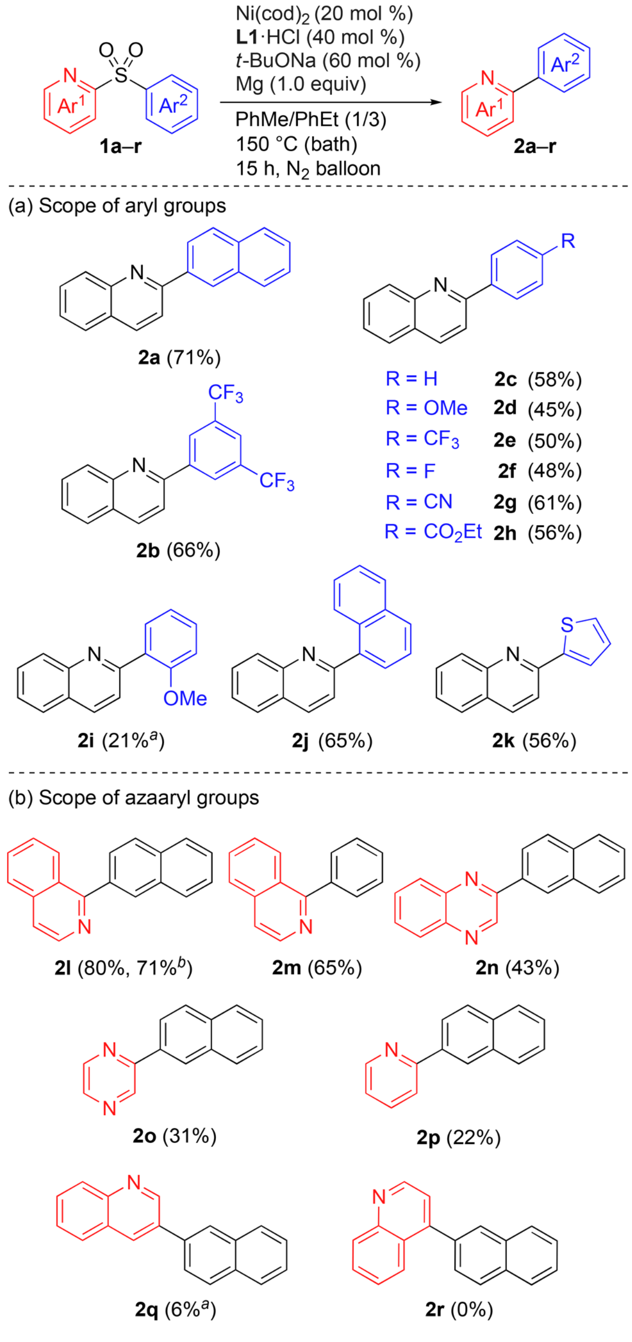
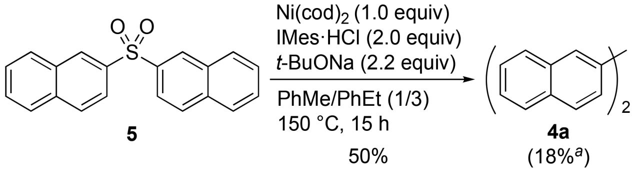
Scheme 2. Scope of Diaryl Sulfones



^{a}Determined by ^{1}H NMR. ^{b}Eight mmol scale.

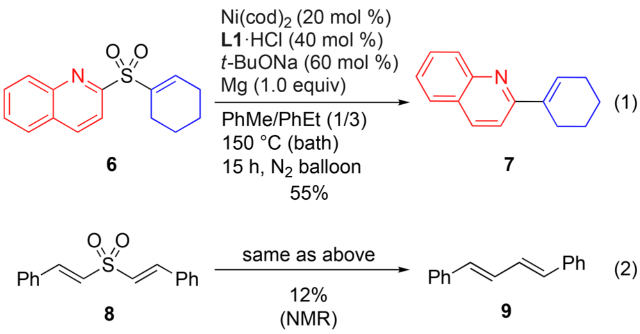
Scheme 3. Intramolecular Desulfitative Coupling of Dinaphthyl Sulfone (5)



^{a}Conditions in Table 1, entry 2. NMR yield.

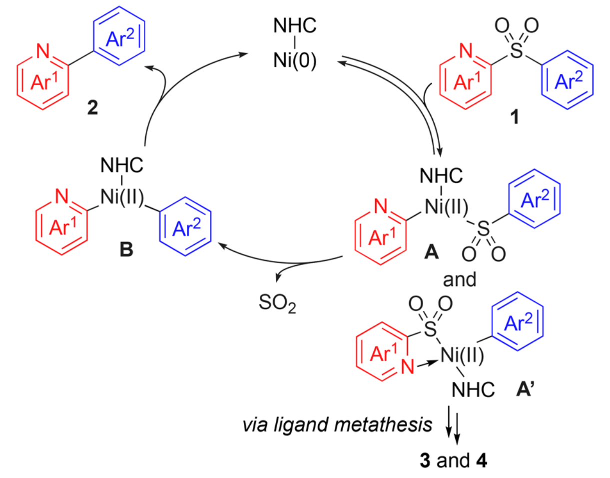
The present intramolecular desulfitative coupling was applicable not only to diaryl sulfones but also to alkenyl aryl sulfone. Under the standard conditions, 1-cyclohexenyl 2-quinolyl sulfone (**6**) could be converted to the desired coupling product **7** in 55% yield (Scheme 4, eq 1). On the other hand, divinyl sulfone **8** which was a suitable substrate in Kamigata's work[8] was not applicable to the present coupling: only a 12% yield of product **9** was obtained, while most of **8** was consumed (Scheme 4, eq 2).

Scheme 4. Intramolecular Desulfitative Coupling of Alkenyl Sulfones



A possible catalytic cycle is shown in Scheme 5. First, a highly electron-rich Ni(0)–NHC complex would cleave one of the two C–SO$_2$ bonds of **1** to provide arylnickel(II) sulfinate **A** and **A′**.[9a−g] Via thermal extrusion of SO$_2$ from these intermediates, diarylnickel(II) species **B** would be then formed. Finally, reductive elimination would afford biaryl **2** and nickel(0) species. The 2-azaaryl ring of **1** is necessary for the smooth desulfitative reaction probably because (1) coordination of the nitrogen to nickel would accelerate oxidative addition and/or (2) the electron-withdrawing nature of the 2-azaaryl ring would thermodynamically stabilize electron-rich diarylnickel **B** to facilitate the desulfitation process.[14] The formation of byproducts **3** and **4** would occur from **A** and **A′**. Intermediate **A** can undergo ligand metathesis[15] with another **A** to afford di(2-azaaryl)nickel and nickel disulfinate. The former would furnish byproduct **3** through reductive elimination. Byproduct **4** would be generated via a similar process from intermediate **A′**.

Scheme 5. Possible Catalytic Cycle



In summary, we have developed intramolecular desulfitative coupling of diaryl sulfones by means of nickel–NHC catalysts. Various aryl 2-azaaryl sulfones underwent the present reaction to afford the corresponding unsymmetrical biaryls in a selective manner. Moreover, this methodology was also applicable to alkenyl aryl sulfone. The intramolecular desulfitative coupling will open up a new avenue for the development of catalytic transformations of sulfonyl compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02972.

Detailed experimental procedures and full spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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