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Ni-Catalyzed Conversion of Enol Triflates to Alkenyl Halides

Julie L. Hofstra†, Kelsey E. Poremba†, Alex M. Shimozono†, and Sarah E. Reisman*

Abstract: A Ni-catalyzed halogenation of enol triflates was developed that enables the synthesis of a broad range of alkenyl iodides, bromides, and chlorides under mild reaction conditions. The reaction utilizes inexpensive, bench stable $Ni(OAc)_2 \cdot 4H_2O$ as a pre-catalyst and proceeds at room temperature in the presence of sub-stoichiometric Zn and either cod or DMAP.

Alkenyl halides are versatile functional groups that can be used in a variety of carbon–carbon and carbon–heteroatom bond-forming reactions. For example, alkenyl halides are commonly used as substrates in transition metal-catalyzed cross-coupling reactions[1] or are converted via metal-halogen exchange to nucleophiles for 1,2-additions to carbonyl compounds (Scheme 1).[2] Furthermore, the alkenyl halide moiety appears in some natural products and bioactive molecules.[3] Whereas acyclic alkenyl halides are easily prepared from the corresponding alkynes[4] or aldehydes,[5] most cyclic alkenyl halides are synthesized from the corresponding ketones. A commonly employed method is the Barton alkenyl halide synthesis (and variations thereof),[6,7,8] which proceeds through an intermediate hydrazone. These reactions are notoriously capricious: the formation of the requisite hydrazone can be challenging on sterically encumbered substrates and the halogenation step often produces mixtures of alkenyl halide isomers or dihalide side products.[9]

As a result, enol triflates, which can be prepared directly from cyclic ketones under either kinetic or thermodynamic control, have emerged as attractive "pseudohalides" for transition metal-catalyzed cross-coupling processes. Unfortunately, enol triflates cannot be directly converted to the corresponding alkenyllithium or alkenylmagnesium species commonly employed in 1,2-addition reactions. In cases where the Barton alkenyl halide synthesis is poor yielding, a multistep alternative is frequently employed: 1) conversion of the ketone to enol triflate, 2) conversion of the triflate to the stannane, and 3) conversion of the stannane to the halide.[10] Direct, mild methods to convert enol triflates to alkenyl halides, without proceeding through organostannane intermediates, can streamline the preparation of these valuable synthons.

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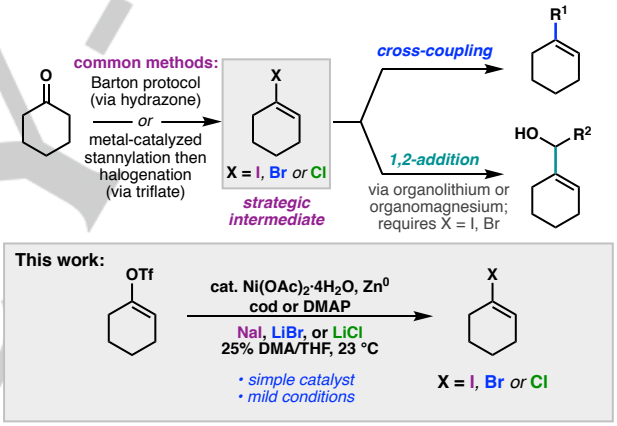
Indeed, Buchwald has reported a Pd-catalyzed reaction to convert alkenyl triflates to alkenyl bromides and chlorides;[11,12] however, there are no examples of alkenyl iodide formation, and the reaction requires an expensive ligand, temperatures greater than 100 °C, and additives such as fluoride salts or $^{i}Bu_3Al$. These additives limit the functional group compatibility of the transformation, particularly with commonly used groups such as silyl ethers. More recently, Hayashi reported a Ru-catalyzed method to convert enol triflates to iodides, bromides, or chlorides that proceeds at ambient temperature; however, the requisite ruthenium catalyst is not commercially available and limited examples of alkenyl iodide formation are reported.[13]



Scheme 1. Synthesis and utility of alkenyl halides.

During our investigations of Ni-catalyzed asymmetric reductive coupling reactions of alkenyl bromides,[14] we observed an off-pathway halide exchange process that generated alkenyl chlorides and iodides. Whereas Ni-catalyzed aryl[15] and alkenyl halide exchange processes have been previously reported and extensively investigated,[15b,16] development of the corresponding reactions of enol triflates have been limited to a single report describing bromination of dihydropyranyl enol triflates.[17,18a] Having observed promising reactivity with enol triflates in our investigation of asymmetric reductive coupling reactions,[19] we hypothesized that an appropriate Ni catalyst and inexpensive halide salts might enable the direct conversion of enol triflates to alkenyl halides under mild conditions. In this communication, we report the development of a Ni-catalyzed triflate-halide exchange (triflex) reaction, which provides access to alkenyl iodides, bromides, and chlorides in good to excellent yields (Scheme 1).

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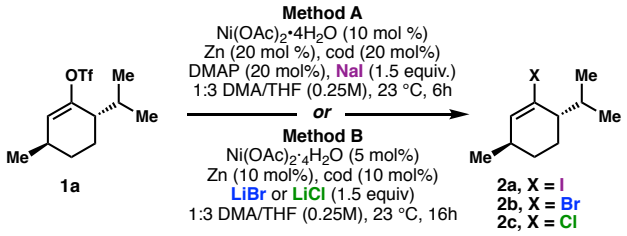
Table 1. Optimization of reaction conditions.[a]



Entry	Deviation from Standard Conditions	Yield **2a** (%)[b]	Yield **2b** (%)[b][c]	Yield **2c** (%)[b][c]
1	None	87	92	90
2	$Ni(acac)_2$	14	85	90
3	NiX_2	75	82	0[d]
4	$Ni(cod)_2$[e]	70	94	94
5	DMA	12	0	0
6	THF	82	69	40
7	DMF	0	18	0
8	MeCN	24	33	8
9	-DMAP (I) / + DMAP (Br/Cl)	33	94	91
10	½ x $Ni(OAc)_2$•$4H_2O$ loading	90	96	94
11	2 x $Ni(OAc)_2$•$4H_2O$ loading	87	94	93

[a] Reactions conducted in 1:3 DMA/THF (0.25M) under inert atmosphere on 0.1 mmol scale. [b] Determined by ^1H NMR spectroscopy versus 1,2,4,5-tetrachloronitrobenzene as an internal standard. [c] Products **2b** and **2c** were found to be volatile. [d] $NiCl_2$ was insoluble under these conditions. [e] No Zn or additional cod were added.

Our reaction development began with enol triflate **1a**, prepared in one step from menthone, with the goal of identifying general conditions that could provide the alkenyl iodide, bromide, or chloride simply by changing the halide salt. Initial optimization efforts using $Ni(cod)_2$ as a catalyst revealed that a mixed DMA/THF solvent system and short reaction times were optimal, and that bidentate ligands (phosphine, amine, and pyridine) inhibited the reaction.[20] Informed by these results, we screened a variety of Ni(II) pre-catalysts in combination with Zn^0 and cod and ultimately found that Ni(OAc)•$4H_2O$ afforded promising yields across all three reactions. Whereas the alkenyl bromides and chlorides could be obtained in good yields in 16 h using 5 mol % $Ni(OAc_2)$•$4H_2O$ and 10 mol % cod (Method B), the iodination proceeded in modest yield under these conditions (Table 1, entry 9). In an effort to improve the yield of the iodination, an additive screen was conducted. This study revealed that use of 20 mol% DMAP, in conjunction with higher catalyst loadings, (10 mol % $Ni(OAc)_4$, 10 mol% cod) improved the yield of **2a**. Since similar yields of **2b** and **2c** are formed in the presence and absence of DMAP (Table 1, entry 9), this additive was omitted for the standard bromination and chlorination conditions (Method B). The precise role of DMAP in the iodination remains unclear; our hypothesis is that it coordinates ZnI_2 salts that are generated as part of the initial Ni(II) reduction.[21, 22, 23] This is consistent with the observation that addition of exogenous ZnI_2 inhibits the reaction, but that reactivity can be restored by addition of DMAP.[20] Although **2a** could be obtained in good yield with 5 mol % Ni (Table 1, entry 10), incomplete conversions were obtained for many substrates when the scope of the iodination was investigated. Increasing the Ni loading to 10 mol % generally improved the conversion and allowed shorter reaction times, which was necessary to minimize the formation of reduction product (Method A).[24]

Having identified satisfactory reaction conditions, the substrate scope of the Ni-catalyzed halogenation reaction was investigated (Table 2). The halide exchange was found to be compatible with a variety of common functional groups, including amines (**4**), carbamates (**5**, **13**), pyridines (**20**), alkenes (**12**), dienes (**10**, **14**), esters (**19**), ketals (**6**, **14**), and enones (**11**). Chemoselective halogenation of alkenyl triflates was observed in preference to aryl triflates (**15**, **20**), aryl chlorides (**9**, **21**), and aryl boronates (**22**); however, competitive halide exchange was observed in the presence of aryl bromides and iodides.[20]

Although the Ni-catalyzed halogenation exhibits good functional group tolerance, the iodination, bromination, and chlorination did not perform equally well. The iodination conditions (Method A) proved optimal for roughly half of the substrates. In cases where iodination was sluggish (**6, 8, 10, 11, 13-16)**, longer reaction times and 5.0 equiv NaI improved conversions; however, the improved reactivity was often accompanied by increased amounts of protodetriflation (or protodehalogenation, approximately 5-10% yield), and the alkene could be difficult to chromatographically separate from the alkenyl iodides (**8a, 10a, 11a, 13a, 15a**). For a subset of these substrates (**10, 11, 13**), the competing reduction was eliminated by use of $Ni(cod)_2$ in conjunction with the enol nonaflate, which afforded access to the pure alkenyl iodides.[18]

The bromination and chlorination reactions were generally more efficient and robust. For most substrates, complete conversions were achieved with 5 mol% Ni and without the need for DMAP, although addition of DMAP improved the yields for substrates where incomplete conversion was observed with only cod (**14-16**). In addition, for 1-arylvinyl triflates (**19-22**, Table 2) the use of $Ni(cod)_2$ (Method C) provided cleaner reaction profiles for the bromination and iodination reactions.[25] To demonstrate the scalability of the reaction, bromide **13b** was prepared in 95% yield on 1 mmol scale using a benchtop setup (**13b**).

At this time, the mechanism of the reaction remains unclear. Preliminary investigations of the iodination using $Ni(cod)_2$ as the catalyst revealed that the reaction of **1a** exhibits an induction period at low [Ni] (e.g. 0.5 mol %, 1 mol %, see Scheme 2a).[26] Plotting V_{max} vs. [Ni] revealed that the reaction has a positive-order dependence on [Ni] that negatively deviates from first order at higher [Ni], suggesting the formation of dimeric (or higher order) off-cycle species at higher [Ni].[27] No change in the rate of iodination of **1a** is observed when the amount of NaI is increased beyond 1 equiv, however the rate

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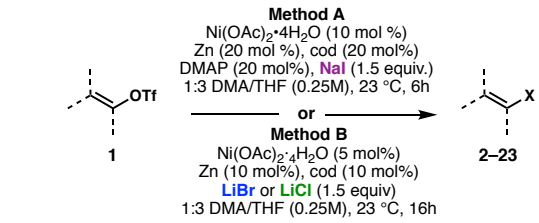
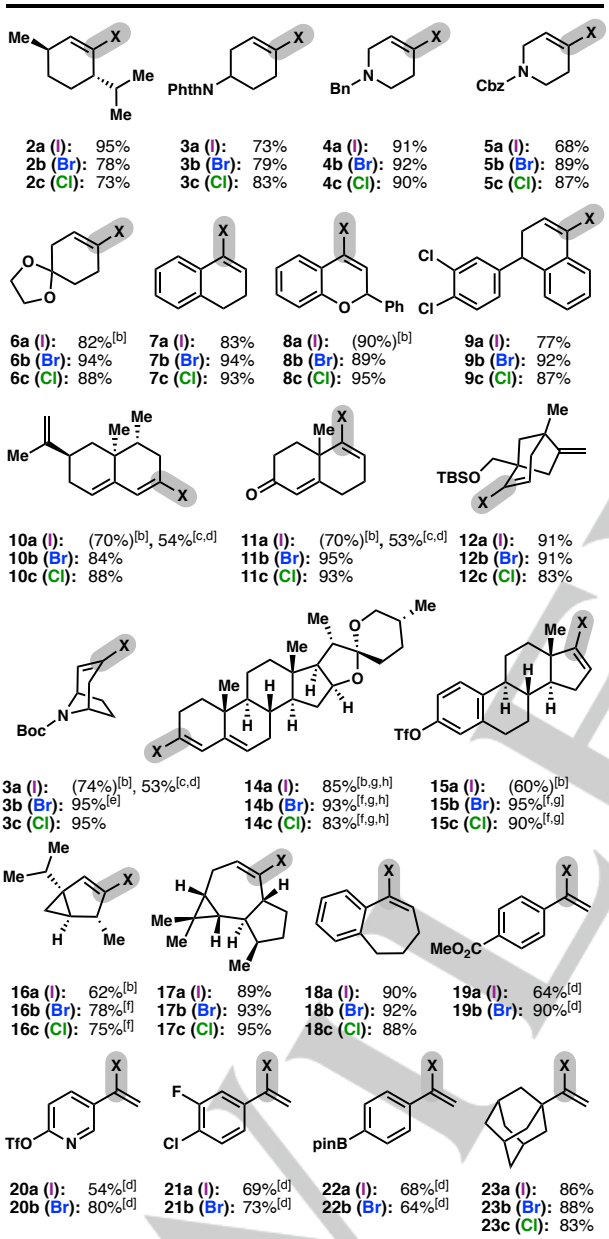
Table 2. Scope of alkenyl halides.[a]



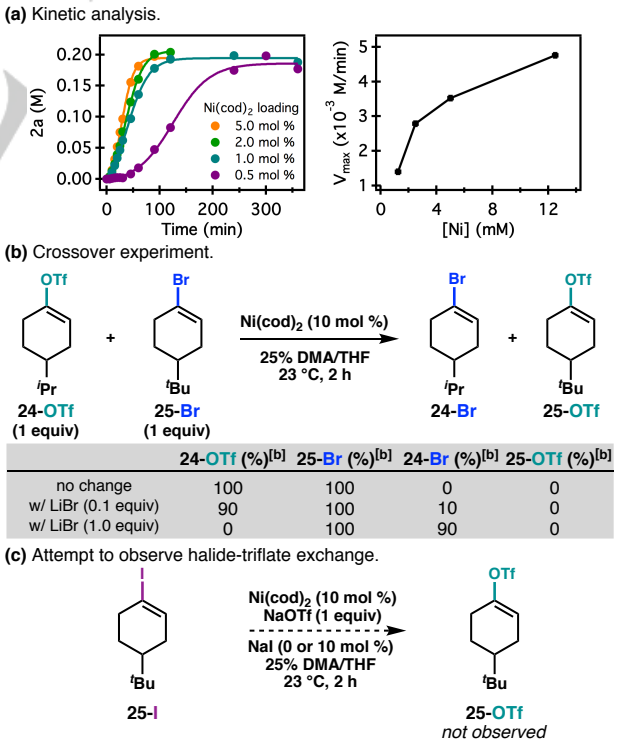


[a] Reactions conducted under inert atmosphere on 0.3 mmol scale. Isolated yields. Yields in parentheses were determined by ^{1}H NMR spectroscopy versus 1,2,4,5-tetrachloronitrobenzene as an internal standard. [b] 5 equiv NaI was used in the absence of cod, 36 h reaction time. [c] Enol nonaflate was employed instead of enol triflate. [d] **Method C:** $Ni(cod)_2$ (10 mol %), MX (1.5 equiv), 25% DMA/THF (0.25M), 23 °C, 16 h. [e] 1 mmol scale, benchtop protocol. [f] DMAP (10 mol %) was used instead of cod. [g] Reaction was conducted on 0.2 mmol scale. [h] Reaction was conducted at 0.125 M due to poor solubility of enol triflate.

dependence on [**1a**] was more complex.[20] One possibility is that the induction period is required to form an active Ni^I catalyst. During the reaction, a signal is present in the EPR spectrum that is consistent with a Ni^I-X species. However, quantification of this signal determined that it was only 2% of the total [Ni], and additional experiments to identify the resting state of the catalyst have been inconclusive.

A crossover experiment was designed to evaluate the reversibility of triflate-halide exchange: treatment of a 1:1 mixture of **24-OTf** and **25-Br** with $Ni(cod)_2$ (10 mol %) in 1:3 DMA/THF at 23 °C resulted in complete recovery of **24-OTf** and **25-Br**, without detection of crossover products **25-OTf** or **24-Br** (Scheme 2b). Addition of 0.1 or 1.0 equiv LiBr resulted in conversion of **24-OTf** to **24-Br** in 10% and 90% yield, respectively;[28,29] no **25-OTf** was detected at any point in either reaction. Monitoring the reaction by ^{1}H NMR spectroscopy confirms that no oxidative addition of **24-OTf** occurs in the absence of halide salt. Subjection of alkenyl iodide **25-I** to $Ni(cod)_2$ (10 mol %) and metal triflate salts (e.g. NaOTf) did not result in enol triflate formation (Scheme 2c).[30] Taken together, these experiments suggest that oxidative addition of the alkenyl triflate is irreversible, or that halide exchange for triflate

Scheme 2. Mechanistic investigation.[a]



	24-OTf (%)[b]	25-Br (%)[b]	24-Br (%)[b]	25-OTf (%)[b]
no change	100	100	0	0
w/ LiBr (0.1 equiv)	90	100	10	0
w/ LiBr (1.0 equiv)	0	100	90	0

[a] Reactions conducted under inert atmosphere on 0.2 mmol scale. [b] Determined by GC analysis versus undecane as an internal standard.

in the oxidative addition complex is rapid and irreversible. In either scenario, the fact that the enol triflate is irreversibly consumed enables the reaction to proceed in good yield to the respective alkenyl halides. This is in contrast to Ni-catalyzed halide exchange reactions, which are thermodynamically driven equilibrium processes.[15b] For example, after 2 h, an 85:15 mixture of **25-Br**:**25-I** is obtained for both the Ni-catalyzed reactions of **25-Br** with LiI, or **25-I** with LiBr.[20]

In conclusion, a mild Ni-catalyzed halogenation of alkenyl triflates has been developed. By modifying the halide salt, alkenyl iodides, bromides, or chlorides can be obtained using a simple, inexpensive catalyst system. These reactions proceed at room temperature, afford the alkenyl halides in good to excellent yields, and exhibit good functional group tolerance.

Acknowledgements

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Keywords: nickel • halogenation • enol triflates • catalysis • alkenyl halides

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arises from the initially formed alkenyl halide and not the enol triflate directly.

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[28] No evidence of oxidative addition is observed when enol triflate **1a** and $Ni(cod)_2$ (5 mol %) were mixed in the presence or absence of NaOTf. However, upon addition of a metal halide salt, conversion of **1a** to the alkenyl halide (**2a-c**) was observed concomitantly with the formation of a Ni(I)-X species. The same Ni(I)-X species were detected upon mixing **2a-c** and $Ni(cod)_2$ (5 mol %). Oxidative addition of aryl triflates to (dppf)Ni(cod) was previously shown to result in Ni(I) complexes via comproportionation: S. Bajo, G. Laidlaw, A. R. Kennedy, S. Sproules, D. J. Nelson, *Organomet.* **2017**, *36*, 1662–1672. (b) I. Kalvet, Q. Guo, G. J. Tizzard, F. Schoenebeck, *ACS Catal.* **2017**, *7*, 2126.

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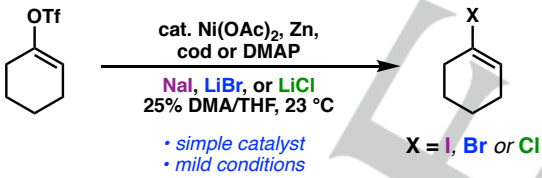

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