Regioselective Synthesis of Vinyl Halides, Vinyl Sulfones, and Alkynes: A Tandem Intermolecular Nucleophilic and Electrophilic Vinylation of Tosylhydrazones

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S *Supporting Information*

ABSTRACT: A diazo species is trapped in an intermolecular fashion by two independent ion species in tandem at the carbene center to install an electrophile and a nucleophile on the same carbon. This metal-free concept, which is unprecedented, has been illustrated by regioselective synthesis of a variety of vinyl halides, vinyl sulfones, and alkyne derivatives.

Hydrazine derivatives are useful intermediates that led to the discovery of Wolf−Kishner reduction and Fisher indole synthesis. Besides Barton vinyl halide preparation,[1] a remarkable transformation of N-alkylsilylhydrozones to their vinyl halides and vinyl *gem*-halides has been documented by Myers.[2] The chemistry of hydrazones for generating carbenes is well addressed, whereas the reaction of hydrazones for generating a sulfinate anion and diazo compounds is understudied. The utility of tosylhydrazones for the formation of C−C bonds has been demonstrated by Barluenga and Wang by trapping a diazo species with boronic acids in an intramolecular fashion to form 1,1-diboron intermediate.[3] This strategy has been exploited for synthesizing a variety of reductive coupling reactions[4,5] and a few interesting tranformations.[6] Trapping the diazo species in an intermolecular fashion by attack of two independent ions (a cation followed by an anion) in tandem at the carbene center is unprecedented. As part of our efforts on the utility of tosylhydrazones,[7] herein we report a novel approach of using ambiphillic diazo species to perform a tandem attack of a nucleophile followed by an electrophile in an intermolecular fashion. In the present work, for the first time, we employ electrophilic and nucleophilic halogen species to develop (i) a convenient method for synthesizing vinyl halides, (ii) a unprecedented method of synthesizing vinyl sulfones by tosyl group transfer, and (iii) a novel strategy of synthesizing alkynes using either tosylhydrazones or ketones. Vinyl halides and vinyl sulfones are easily amenable for a variety of transformations[8] and are versatile precursors and key fragments for several drug molecules. Although the transformation of hydrozones that contain free NH$_2$ to their corresponding haloolefins are known, the present method is more convenient as tosylhydrazone derivatives are easy to handle.

The reaction of N-tosylhydrazone of 4-methoxy acetophenone (**1**) with an electrophilic chlorine source N-chlorosuccinimide (NCS) and a nucleophilic bromine source, tetrabutylammonium bromide (TBAB) resulted in the formation of a mixture of corresponding vinyl bromide and vinyl chloride in a 6:4 ratio (Scheme 1). This result invoked the involvement of the
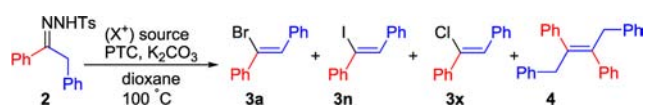
Scheme 1. Trapping Diazo Species
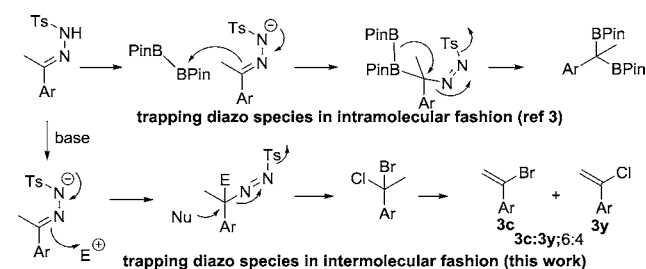
corresponding dihalide derivative 1-(1-bromo-1-chloroethyl)-4-methoxybenzene (Scheme 1), which upon treatment with base formed a mixture of vinyl bromide and vinyl chloride. Tosylhydrazone of 1,2-diphenylethanone (**2**) and a combination of NBS (N-bromorosuccinimide) as electrophilic halogen source and TBAB as nucleophilic halide source were used in screening studies. The reactions in the absence of either NBS or TBAB did not yield the expected product, whereas the NBS−TBAB has emerged as a useful combination in the presence of a variety of bases to furnish the product (Z)-(1-bromoethene-1,2-diyl)-dibenzene **3a** (entries 1−9). The combination of NIS and tetrabutylammonium iodide (TBAI) afforded the corresponding iodo derivative **3n** in 82%, whereas catalytic amount of TBAB or excess of NaBr was not helpful (entries 10−12). Molecular bromine or iodine was not effective as halonium ion sources, while the combinations of NBS or NCS with TBAI resulted in the formation of a mixture of products (entries 13−16). Thus, the optimal reaction conditions for obtaining vinyl halides

require NBS (1.5 equiv), TBAB (3 equiv) and K$_2$CO$_3$ (3 equiv, entry 8). Similar output was observed with Cs$_2$CO$_3$ (entry 9), but due to moisture sensitivity and cost effect, former condition was followed as the standard reaction conditions.

Table 1. Optimization Studies[a]

entry	(X$^+$) source (equiv)	additive (equiv)	base	yield (%)[b] 3:4
1	NCS (1)	none	K$_2$CO$_3$	nd
2	none	TBAB (1)	K$_2$CO$_3$	nd
3	NBS (1)	TBAB (1)	K$_2$CO$_3$	39:60[c]
4	NBS (1)	TBAB (1.5)	K$_2$CO$_3$	47:45[c]
5	NBS (1)	TBAB (1.5)	Et$_3$N	10:90[c]
6	NBS (1)	TBAB (1.5)	NaOMe	60:38[c]
7	NBS (1)	TBAB (3)	K$_2$CO$_3$	68:30[c]
8	**NBS (1.5)**	**TBAB (3)**	**K$_2$CO$_3$**	**90:00**[c]
9	**NBS (1.5)**	**TBAB (3)**	**Cs$_2$CO$_3$**	**93:00**[c]
10	NIS (1.5)	TBAI (3)	K$_2$CO$_3$	82:00[d]
11	NBS (1)	TBAB (0.1)	K$_2$CO$_3$	trace
12	NBS(1.5)	NaBr (3)	K$_2$CO$_3$	nd
13	Br$_2$ (1)	none	K$_2$CO$_3$	nd
14	I$_2$ (1)	none	K$_2$CO$_3$	nd
15	NBS (1.5)	TBAI (3)	K$_2$CO$_3$	62:00[e]
16	NCS (1.5)	TBAI (3)	K$_2$CO$_3$	61:00[f]

[a]Reaction conditions: **1a** (1 mmol), NBS (1.5 equiv), TBAB (3 equiv), K$_2$CO$_3$ (3 equiv), dioxane (3 mL), 90 °C, 8−12 h. [b]Isolated yields. [c]**3**:**4**. [d]**3n**:**4**. [e]**3a**:**3n** was formed in 60:40 ratios. [f]**3n**:**3x** was formed in 71:29 ratio.

A variety of hydazones underwent a smooth transformation under the optimal reaction conditions to furnish the corresponding vinyl halides in good to excellent yields (Scheme 2). Tosylhydrazone of 4-methylacetophenone and 4-methoxyace-

Scheme 2. Synthesis of Vinyl Halides[a,b]
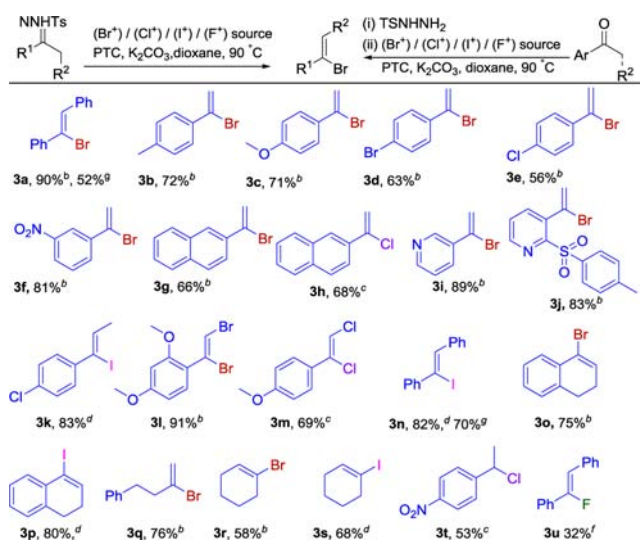
[a]Reaction conditions: halonium source (1.5 equiv), PTC (2.5 mmol), **2a** (1 mmol), K$_2$CO$_3$ (3 mmol), dioxane (3 mL), 90 °C, 8−12 h. [b]NBS (1.5 mmol), TBAB (3 mmol). [c]NCS (1.5 mmol), BTEAC (3 mmol). [d]NIS (1.5 mmol), TBAI (3 mmol). [e]Isolated yields. [f]NFSI (1.5 mmol), TBAF (3 mmol). [g]In situ reactions.

tophenone in a reaction with NBS−TBAB combination furnished the corresponding vinyl bromide **3b** and **3c** in 72 and 71%, whereas tosylhydrazone derivatives that are substituted with halo or nitro groups afforded the corresponding vinyl bromides **3d**, **3e**, and **3f**, respectively in good to moderate yields (63, 56, and 81%, respectively). The reaction of the hydrazone of 1-(naphthalen-2-yl)ethanone with NBS−TBAB and NCS−BTEAC (benzyltriethylammonium chloride) combinations proceeded well to furnish the corresponding vinyl halides **3g** and **3h** in good yields (66 an 68%, respectively). Notably, bromo vinylpyridines **3i** and **3j** are obtained in good yields (89, and 83%, respectively), while the reaction of the hydrazone derivative of 4-chloropropiophenone with NIS−TBAI furnished the corresponding vinyl iodide **3k** in good yield (83%). Hydrazone derivatives of phenacyl halides afforded the corresponding vinyl dibromide (**3l**) and vinyl dichloride (**3m**) in 91 and 69% yields, respectively. As expected, hydrazine derivatives of 1,2-diphenylethan-1-one yielded the corresponding vinyl iodide **3n** in 82% yield, and hydrazones of tetralone reacted well with NBS−TBAB or NIS−TBAI combination to afford the corresponding vinyl bromide **3o** and vinyl iodide **3p** in excellent yields (75 and 80%, respectively). This strategy is also compatible with tosylhydrazones of aliphatic ketones, such as 4-phenyl-butan-2-one and cyclohexanone, which in reaction with NBS−TBAB or NIS−TBAI combination furnished the corresponding aliphatic vinyl halides **3q**, **3r**, and **3s** in good yields (76, 58, and 68%, respectively). However, the hydrazone of 1-(4-nitrophenyl)ethanone with NCS-BTEAC formed 1-(1- chlor-oethyl)-4-nitrobenzene (**3t**) in moderate yield (53%), which can be attributed to the inability of the nitro derivative to form the corresponding geminal dichloride. Interestingly, the reaction was also useful in synthesizing (Z)-(1-fluoroethene-1,2-diyl)-dibenzene (**3u**) in low yield (32%), which was performed using N-fluorobenzenesulfonimide NFSI)/tetrabutylammo-niumfluoride (TBAF) combination. The application of this reaction has been emphasized using the ketones as the precursors in single pot to form the corresponding vinyl bromide (**3a**) and vinyl iodide (**3n**) in moderate to good yields (52 and 70%, respectively).

In the reaction of **2**, when the bromonium species was switched over to bromine radical using CNBr, the reaction took completely unexpected turn and furnished the corresponding vinyl sulfone **5a** in excellent yield (93%). The formation of vinyl sulfone can be explained by the initial reaction of tosyl hydrazone with CNBr to form α-bromo azo derivative, which extrudes nitrogen to form gem-bromo sulfone derivative. The bromo-sulfone derivative thus formed undergoes a 1,2 halo sulfone rearrangement[9] to furnish the corresponding vinyl sulfones. The reports on the migration of tosyl group are rare and unprecedented.[10] A variety of tosylhydrazone derivatives found to undergo this reaction with CNBr−TBAB combination in the presence of K$_2$CO$_3$ at 100 °C in dioxane and furnish their corresponding vinyl sulfones (Scheme 3). Vinyl sulfones are potential synthetic targets due to their presence in biologically and pharmaceutically active molecules,[11] which are generally synthesized through elimination reactions, oxidation of vinyl sulfides or witting reactions using multistep sequences.[12] Whereas, the present method offers an advantage of synthesizing vinyl sulfones in a single pot reaction from ketones or tosylhydrazones using inexpensive common reagents. This reaction proceeded well with a variety of hydrazone derivatives to furnish the corresponding vinyl sulfones **5b**, and **5c** in excellent yields (89 and 95%, respectively). The regiochemistry

Scheme 3. Synthesis of Vinyl Sulfones[a,b]
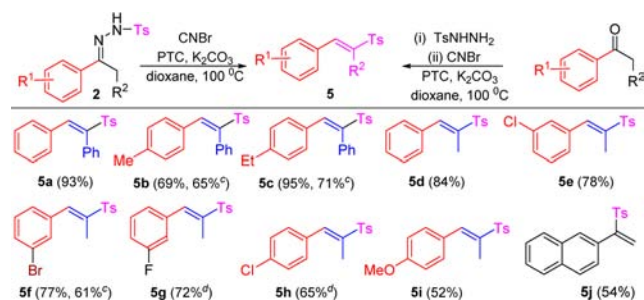
[a]Reaction conditions: 2a (1 mmol), CNBr (1.1 mmol), TBAB (2.5 mmol), K$_2$CO$_3$ (3 mmol), dioxane (3 mL), 100 °C, 8−12 h. [b]Isolated yields. [c]In situ experiment from ketone. [d]E-Geometry was confirmed by 1D NOE experiments.

of **5b** and **5c** was confirmed by 2D experiments (see SI-Scheme 3, Supporting Information). Further, the reactions of tosylhydrazone derivatives of halo-substituted aromatic ketones proceeded smoothly to furnish the corresponding vinyl sulfones **5d**, **5e**, **5f**, **5g**, and **5h** in good yields (84, 78, 77, 72, and 65%, respectively).

Similarly, the tosylhydrazone derivative of 1-(4-methoxyphenyl)propan-1-one reacted well with CNBr-TBAB to yield the corresponding vinyl sulfone **5i** in 52% yield. The formation of *E*-vinylsulfones has been confirmed by 1D NOE experiment (see SI-Scheme-2, Supporting Information). The utility of this novel reaction has been illustrated in a single pot reaction of ketones to obtain the corresponding sulfones **5b**, **5c**, and **5f** in good yields (85, 71, and 61%, respectively). However, the silmiar reaction of CNBr−TBAB with acetophenone was not successful. Nevertheless, the reaction of 2-acetylnapthalene with CNBr−TBAB combination furnished the sulfone **5j** (54%) in which migration of tosyl group was not observed. Interestingly, under a controlled reaction conditions, the reaction of tosylhydrazone of 1-(3-chlorophenyl)propan-1-one, 1-(3-bromophenyl)propan-1-one, and 1-(4-chlorophenyl)propan-1-one furnished the corresponding halosulfones **6a**, **6b**, and **6c** in 37, 56, and 51%, respectively (Scheme 4). Formation of these bromo sulfones strongly

Scheme 4. Synthesis of Halo Sulfones
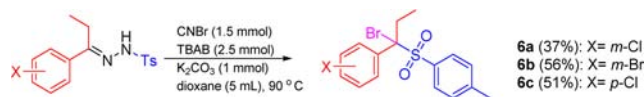
supports our speculations that these reactions are proceeding via the correspoinding bromoderivatives, which was confirmed by an independent reaction of **6a** in basic media which led to the formation of rearranged sulfone **5e**.[13]

The formation of geminal dihalide as an intermediate in the reaction of hydrazone with NBS and TBAB (Scheme 1) motivated us to undertake an investigation for synthesizing the corresponding alkynes. Synthesis of alkynes from ketones via carbenes is an untapped research area. The present protocol provides a novel and unprecedented avenue for accessing alkynes from hydrazones as well as ketones. After extensive screening studies, it was pleasing to find that the reaction of tosylhydrazone **2** with NCS−BTEAC, NBS−TBAB, or NIS−TBAI combination in the presence of K$_2$CO$_3$ in dioxane at 110 °C furnished diphenylacetylene **7a** in 71, 67, and 63%, yields, respectively (Scheme 5). The tosylhydrazone derivatives of 1-(4-ethyl-phenyl)-2-phenylethan-1-one and 2- phenyl-1-(*p*-tolyl)ethan-1-

Scheme 5. Synthesis of Alkynes[a]
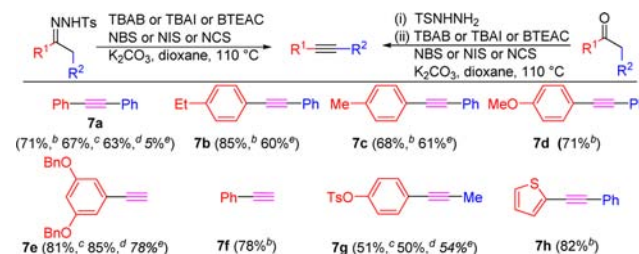
[a]Reaction conditions: 2a (1 mmol), halonium source (1.5 mmol), PTC (3 mmol), K$_2$CO$_3$ (3 mmol), dioxane (3 mL), 110 °C, 8−12 h. [b]NCS/BTEAC conditions. [c]NBS/TBAB conditions. [d]NIS/TBAI conditions. [e]In situ experiment from ketone.

one underwent a facile reaction to furnish the corresponding alkynes **7b** and **7c** in 85 and 68%, respectively. Alkoxy substititiuon on the phenyl rings did not affect the reaction and the alkyne **7d** was obtained in 71% yield. The terminal alkynes such as **7e** and **7f** can be accessed using this method in excellent yields (81 and 78%, respectively). The tosylhydrazone derivatives of 1-(4-hydroxyphenyl)propan-1-one formed the corresponding acetylene derivative **7g** in moderate yield (51%), wherein phenolic hydroxy group is also tosylated. The hydrazones derivative of heterocyclic ketone such as 2-phenyl-1-(thiophen-2-yl)ethan-1-one with NCS−BTEAC yielded the corresponding alkyne **7h** in 82% yield. Finally, a one-pot reaction of ketones under the optimal conditions proceeded well to furnish the corresponding alkynes **7a**, **7b**, **7c**, **7e**, and **7g** in 55, 60, 61, 78, and 54%, respectively.

The compatibility of this reaction was studied using the protocol developed by Glorius (see SI-Table 1, Supporting Information).[14] Although isoquinoline survives the reaction conditions, the yield of the product is reduced by almost half. Styrene gets consumed during the reaction without affecting the yield of the product indicating olefins are not tolerated under the reaction conditions. Pyridine oxide is detrimental to the reaction as formation of product was not observed. Benzoic acid has been consumed and reduces the yield, suggesting that the reaction does not tolerate the acid functionality. Benzenesulfonyl azide has almost no effect on the reaction, but gets destroyed under the reaction conditions.

In order to understand the mechanism, a few control experiments were performed. Based on these experiments (see SI-Scheme 4, Supporting Information), we postulate that the reaction of tosylhydrazone **2** with NBS−TBAB follows ionic mechanism, whereas the reaction of **2** with CNBr−TBAB to form sulfones proceeds through radical mechanism (Scheme 6). The tosylhydrazone **2** in the presence of base generates the diazo

Scheme 6. Plausible Reaction Mechanism
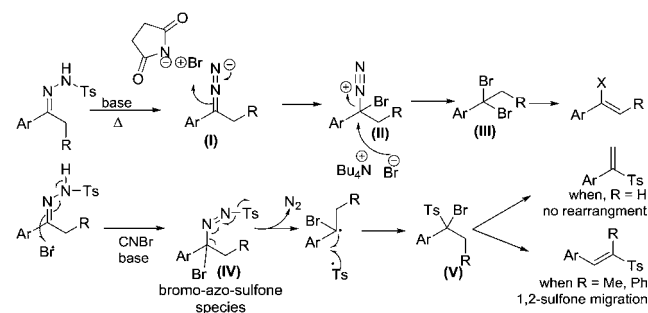
intermediate **I**, which reacts with NBS to form **II**. Further **II** reacts with TBAB to afford the dibromide **III** (which was isolated). Under heating conditions, **III** loses HBr to furnish the corresponding vinyl halide. Further, the reaction of preformed diazo compound (1-(1-diazoethyl)-4-methoxybenzene) under optimal conditions has resulted in the formation of corresponding vinyl bromide **3c** in 51% indicating the intermediacy of diazo species (see SI-Scheme 5, Supporting Information). In the reaction of CNBr–TBAB, with the bromine radical reacts with **2** to form **IV** which upon extrusion of N_2 followed by migration of tosyl group forms the stable intermediate **V**, which was isolated in an independent experiment. The tosyl group migration in these reactions has been further confirmed by performing a mixed reaction of two sulfonyl hydrazine derivatives with CNBr–TBAB under the optimal conditions, which yielded a mixture of sulfone products (see SI-Scheme 6, Supporting Information).[15] Based on this information, we believe that the intermediate **V** undergoes dehydrohalogenation to furnish the corresponding vinyl sulfones, which was also isolated in an independent experiment (see SI-Scheme 7, Supporting Information). A further study to follow the formation of alkynes is underway in our laboratory.

It has been demonstrated that it is possible to trap the diazo species in an intermolecular fashion by attack of two independent ion species in tandem at the carbene center to install an electrophile and a nucleophile on the same carbon. This process has led to the formation of a *gem*-dihalide intermediate followed by vinyl halides. Further, the reaction of tosylhydrazone with CNBr and aliphatic quarternary ammonium salts has resulted in the formation of vinyl sufones, in which the migration of a tosyl group has been witnessed for the first time. A novel avenue for synthesizing alkynes from hydrazones as well as ketones has thus been revealed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization data, and spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) See the Supporting Information for the proposed reaction mechanism of 1,2-migration of the sulfone moiety (see SI-Scheme 8, Supporting Information).

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(15) See the Supporting Information for the mixed experiment and proposed reaction mechanism. We are thankful to anonymous referees for useful suggestions.