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Brønsted Acid Catalyzed Friedel-Crafts-type Coupling and Dedinitrogenation Reactions of Vinyldiazo Compounds

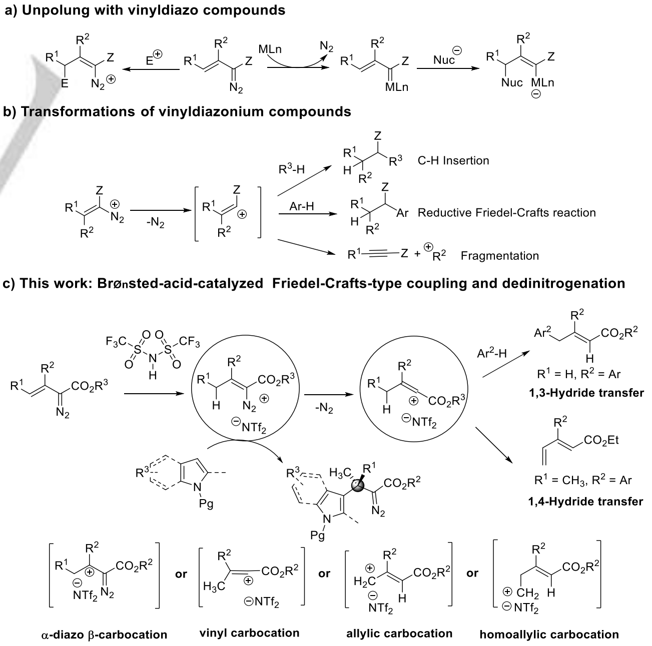
Haifeng Zheng, Kuiyong Dong, Daniel Wherritt, Hadi Arman, Michael P. Doyle*

Abstract: The direct Friedel-Crafts-type coupling and dedinitrogenation reactions of vinyldiazo compounds with aromatic compounds using a metal-free strategy are described. This acid-catalyzed methodology is efficient for the formation of α-diazo β-carbocations (vinyldiazonium ions), vinyl carbocations, and allylic or homoallylic carbocation species *via* vinyldiazo compounds. By choosing suitable nucleophilic reagents to selectively capture these intermediates, both trisubstituted α,β-unsaturated esters, β-indole-substituted diazo esters, and dienes are obtained in good to high yields and selectivities. Experimental insights implicate a reaction mechanism involving the selective protonation of vinyldiazo compounds and the subsequent release of dinitrogen to form vinyl cations that undergo intramolecular 1,3- and 1,4- hydride transfer processes as well as fragmentation.

Vinyldiazo compounds are prominent building blocks for organic synthesis.[1] Their dipolar nature makes them susceptible to electrophilic addition, but when transformed to their carbenic state, especially as metallocarbenes, the vinylcarbenes are electrophiles (Scheme 1a, right),[2] and their role as electrophiles has revealed a diversity of cycloaddition reactions, accessing carbocyclic and heterocyclic compounds via [3+*n*]-transformations with rhodium(II),[3] copper(I),[4] and gold(I)[5] catalysts. In contrast, vinyldiazo compounds are also effective nucleophiles that undergo cycloaddition reactions with electrophiles to produce increasingly complex structures, dependent on the nature of the electrophiles,[6] and they have the potential to offer complimentary processes to those of metal carbenes. However, synthetically effective cationic addition reactions with vinyldiazo compounds have not been explored (Scheme 1a, left).

Although viable catalytic methods involving protonation of diazo compounds to afford diazonium ions are well established,[7] this strategy has not been applied to easily accessible and stable vinyldiazo compounds. Vinyl carbocations[8] formed by loss of dinitrogen are intriguing reactive intermediates that have gained increasing attention in recent years,[9] and the carbene-like reactivity of cyclic vinyl cations has been uncovered,[10-15] revealing ring-expansion/contraction,12 inter- and intra-molecular C-H insertion,[13,14] as well as fragmentation reactions (Scheme 1b).[15a] In the only previous example of an acyclic system that generated a vinyldinyldiazonium ion, 1-(ethoxycarbonyl-diazomethyl)-2-phenylisopropyl alcohol was treated with 150 mol% of $BF_3{\bullet}Et_2O$ under various conditions to form between five and nine products.12 Inspired by these reports, we postulated that a suitable Brønsted acid could undergo proton addition to a vinyldiazo compound to produce a vinyldiazonium ion, which is itself susceptible to nucleophilic trapping, that upon releasing dinitrogen delivers the corresponding weakly coordinating counter ion-stablized vinyl carbocation for subsequent transformations.

We have discovered that bis(trifluoromethanesulfonyl)imide ($HNTf_2$) serves as a uniquely efficient Brønsted acid that selectively protonates the vinylogous position of vinyldiazo compounds forming a vinyldiazonium ion. Further transformation into vinyl and allylic or homoallylic carbocation intermediates occurs via sequetial loss of dinitrogen and hydride transfer, realizing catalytic Friedel-Crafts-type coupling and dedinitrogenation transformations. The strong acidity of triflimide, as well as the low nucleophilicity and weak coordination of its counter anion Tf_2N^-, allows this superacid to serve as an exceptional catalyst in a wide range of organic reactions,[16] but none have been reported with diazo compounds. In this metal free strategy, both α,β-unsaturated esters, β-indole substituted diazo esters, and dienes are obtained in good yields and selectivities (Scheme 1c).



Scheme 1. Background and this work.

Phenylvinyldiazoacetate **1a** and benzene **2a** were selected as model substrates to evaluate the title reaction. Commercially available Brønsted acids, such as CH_3COOH and H_2SO_4 were initially employed as catalysts, but no cross-coupled products were obtained (Table 1, entries 1 and 2). However, when

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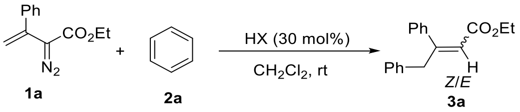
CF_3COOH or TfOH were used to effect this transformation, 3-phenyl vinyl diazoacetate **1a** was slowly consumed, and, surprisingly, α,β-unsaturated ester **3a** was isolated (Table 1, entries 3 and 4), albeit in low yield. There was no trace of product (ethyl 2,3-diphenyl-2-butenoate) anticipated from direct reaction with the vinyl cation. Futher optimization with different acids demonstrated that superacid $HNTf_2$, with the low nucleophilicity and coordinating ability of its conjugate base (Tf_2N^-),[16] was the most efficient catalyst; product **3a** was obtained in 81% yield with 8:1 *Z*/*E*-selecticity (Table 1, entry 5). The *Z*/*E* stereoisomers could be separated chromatographically, and Z-**3a** was obtained in 72% isolated yield. Attempts to optimize the yield of **3a** by decreasing the temperature were unsuccessful (Table 1, entry 6) and reducing the catalyst loading (Table 1, entry 7), while prolonging the reaction time, did not provide full consumption of the **1a**.

Table 1. Optimization of reaction conditions for coupling of **1a** and **2a**.[a]



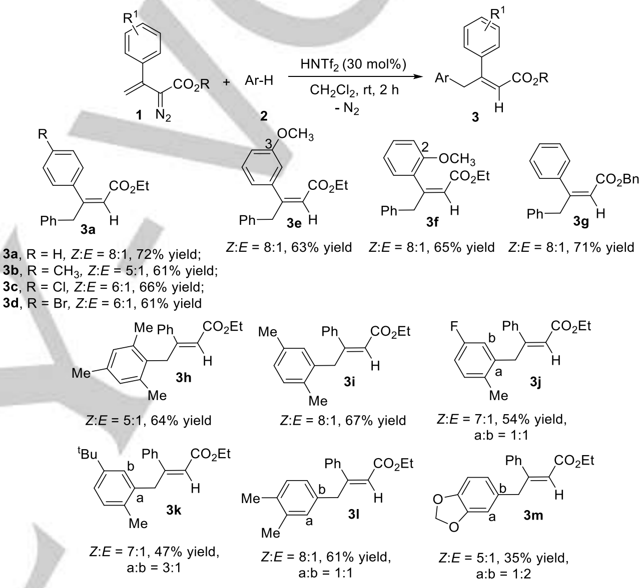
Entry[a]	HX (30 mol %)	Conditions	Z/E[b]	Yield of *Z*-**3a** (%)[c]
1	CH_3COOH	rt, 12 h	-	-
2	H_2SO_4	rt, 12 h	-	-
3	CF_3COOH	rt, 12 h	4:1	20
4	TfOH	rt, 12 h	4:1	23
5	$HNTf_2$	rt, 2 h	8:1	72
6	$HNTf_2$	0 °C, 12 h	8:1	42
7[d]	$HNTf_2$	rt, 12 h	8:1	56

[a] Reactions were performed by adding **1a** (0.2 mmol) to HX (30 mol%) in benzene/CH_2Cl_2 solvent (v:v = 1:1, 2 mL). [b] *Z*/*E* ratio was determined by ^1H NMR analysis of the reaction mixture. [c] Yields of isolated *Z*-**3a** product. [d] 20 mol% $HNTf_2$ catalyst loading.

With optimized conditions in hand, we examined the scope of Friedel-Crafts-type coupling reactions of β-aryl substituted vinyldiazo esters **1** with arenes **2** (Scheme 2). Both moderately electron-withdrawing and electron-donating substituents on the para-position of the phenyl ring of **1** were compatable with the formation of α,β-unsaturated esters *Z*-**3b**-*Z*-**3d** in good yields and selectivities. Furthermore, substituents at different positions of the phenyl ring had little effect on the reaction (**3e** and **3f**). Benzyl ester **1g** also underwent Friedel-Crafts coupling with benzene **2a** in good yield and selectivity without debenzylation. However, analogous β-alkyl substituted vinyldiazo compounds did not produce any of the desired coupling products (for details, see Supporting Information), possibly due to the instability of these vinyl carbocation intermediates. The substrate scope of arenes **2** for this Friedel-Crafts reaction was also explored (Scheme 2). Symmetric mesitylene **2b** and *p*-xylene **2c** underwent this reaction, and the corresponding products **3h** and **3i** were obtained in good yields. Arenes **2d**-**2f** were suitable substrates (**3j**-**3m**, 35%-61% yields, 5:1-8:1 *Z*/*E* selectivities), but their regioselectivities were not remarkable (1:1-3:1).

Based on the successful coupling with arenes and vinyldiazo compounds, we investigated their use in this metal-free strategy with the more nucleophilic indoles. In a reaction performed at room temperature with catalytic $HNTf_2$ the β-indole substituted diazo ester **5a** was isolated in 68% yield, consistent with nucleophilic trapping of a vinlyldiazonium ion. The absence of these similar diazo compounds in reactions with arenes like anisole with its strong electron-donating substituent suggests that there is a threshold in nucleophilicity for substrates that can trap the vinyldiazonium ion prior to its release of dinitrogen to form the vinyl cation. The scope of this Friedel-Crafts coupling reaction with indoles **4** (Scheme 3, top) showed that the 3-aryl substituent of vinyldiazo compounds **1** bearing an electron-donating substituent provided a higher yield than that with an electron-withdrawing group (EWG) (**5b** versus **5c**). Furthermore, substituents at different positions of the phenyl ring (**1e** and **1f**) and the ester substituent **1g** had a little influence on the reaction (**5d**-**5f**). The β-alkyl substituted vinyldiazo compounds (R = Me, Et, *n*-Pr; **1h**-**1j**) showed higher reactivities than β-aryl substituted substrates in this coupling reaction, and the catalyst loading could be reduced to 2.5 mol% (**5n**-**5p**).

Scheme 2. Scope of the $HNTf_2$-promoted Friedel-Crafts-type coupling of arenes and vinyl diazo compounds.[a]



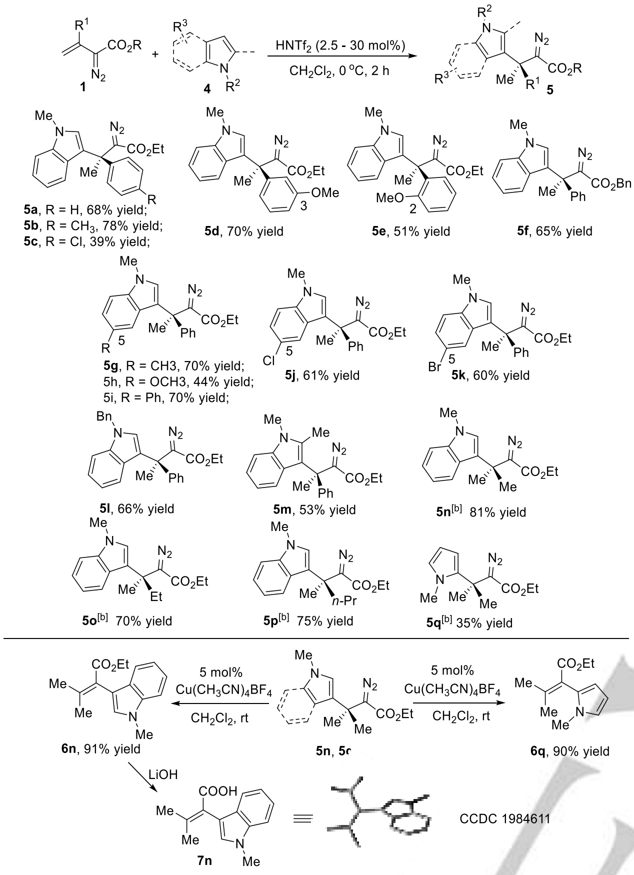
[a] Reactions were performed by adding **1** (0.3 mmol) to $HNTf_2$ (30 mol%) in arene/CH_2Cl_2 solvent (v:v = 1:1, 3 mL), unless otherwise noted: *Z*/*E* ratio was detected by crude ^1H NMR spectroscopy; Yield was for the isolated *Z* product.

Both electron-withdrawing and electron-donating substituents on the indole ring produced the corresponding products (**5g**-**5k**, 44%-70% yield) in good yields, the lowest yield being due to decomposition of 5-methoxy-substituted indole **4c** with $HNTf_2$. *N*-Benzyl substituted indole **4g** was a suitable substrate (**5l**, 66% yield), but the *N*-H substituted indole did not form the coupling product (for details, see Supporting Information). Furthermore, 1,2-dimethylindole **4m** and pyrrole **4i** underwent this transformation smoothly. However, attempts with other heterocyclic compounds, including furan, benzofuran and phenol, were not successful.

The diazo esters formed from indoles and pyrroles by this process have a quaternary carbon adjacent to the diazo carbon in which all of the attachments are carbon. These compounds are susceptible to 1,2-migration in transition metal catalyzed processes,[1a] that opens a pathway to tetrasubstituted alkenes. [17] The $[Cu(CH_3CN)_4][BF_4]$ catalyzed indole migration of **5n** and **5q** to tetra-substituted alkenes **6n** and **6q** occur in excellent yields

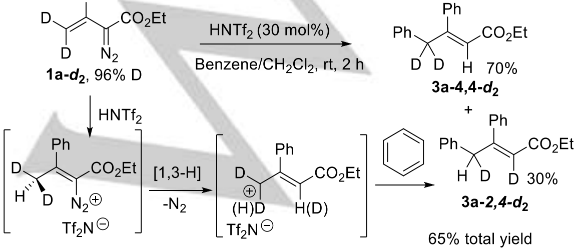
(Scheme 3, bottom). The structure of **6n** was demonstrated by X-ray diffraction of its derivative **7n** (Scheme 3, bottom).[18]

Scheme 3. Scope of the HNTf$_2$-promoted Friedel-Crafts-type coupling of indoles and vinyl diazo compounds.[a]



[a] Reactions were performed by adding HNTf$_2$ (30 mol%) to **1** (0.3 mmol) and **4** (0.2 mmol) in CH$_2$Cl$_2$ solvent (4 mL) at 0 °C, unless otherwise noted: Isolated yield after chromatography. [b] 2.5 mol% catalyst loading.

To better understand the mechanism of the Friedel-Crafts-type coupling reactions we performed duterium-labeling studies to follow the hydride-transfer reaction. Deuterium labeled substrate **1a-d_2** was prepared and treated with Tf$_2$NH under the standard reaction conditions (Scheme 4). Products **3a-2,4-d_2** and **3a-4,4-d_2**, formed from **1a-d_2** in a ratio of 3:7 (Scheme 5a), result from selective protonation the vinylogous position of the vinyldiazo compound by Tf$_2$NH and subsequent 1,3-H/D transfer. Since the methyl group formed by proton addition from Tf$_2$NH possesses two deuterium and one proton, the **3a-4,4-d_2/3a-2,4-d_2** product ratio provides an estimate of the product isotope effect (4.7).



Scheme 4. 1,3-Hydride transfer determined from labeling experiment.

Based on the experimental results for these reactions, we propose in Figure 1 the probable mechanism of HNTf$_2$ catalyzed Friedel-Crafts-type coupling reactions of vinyldiazo compounds. The reaction is initiated by protonation of vinyldiazo compounds **1** with HNTf$_2$ to give the corresponding vinyldiazonium ion intermediate **int-I**, which is captured by nucleophilic indoles and pyrrole affording substituted diazo esters **5**. In the absence of a nucleophile suitable to trap the vinylydiazonium ion, β-aryl substituted **int-I** releases dinitrogen either stepwise through the vinyl carbocation (**int-II)** or synchroneously to form the allylic carbocation **int-III** by 1,3-hydride transfer, which undergoes the Friedel-Crafts alkylation of arenes.

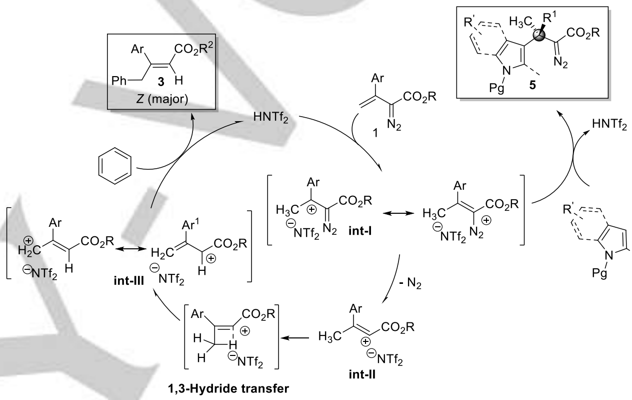


Figure 1. Proposed mechanism for Friedel-Crafts-type coupling.

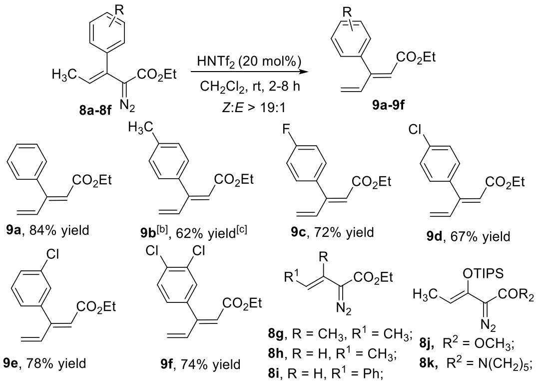
A different outcome occurred when γ-methyl substituted vinyldiazo compound **8a** was subjected to HNTf$_2$ catalysis in the absence of a nucleophile. From prior results with vinyl cations we expected that an intramolecular carbene-like C-H insertion [13] might occur, possibly affording a cyclobutene derivative, but diene **9a** was isolated in 84% yield with excellent *Z*-selectivity (Scheme 5). The same product was formed exclusively when the reaction of **8a** with Tf$_2$NH was performed in benzene; no Friedel-Crafts alkylation product was detected. These results suggested a reaction process involving either or both allylic and homoallylic carbocation intermediates. In addition, the substrate scope shows that both moderately electron-withdrawing and electron-donating substituents on the 4-position of phenyl ring of vinyldiazo compound favor production of the corresponding dienes (**9b**-**9f**) in good yields with excellent selectivities (Scheme 5). However, β-alkyl (**8g**) and β-hydrogen (**8h** and **8i**) substituted vinyldiazo compounds were not suitable reactants for this transformation, affording complex product mixtures; and treatment of triisopropylsilyl (TIPS) protected enoldiazoacetate **(8j)** and enoldiazoacetamide (**8k**) with HNTf$_2$ only gave the desilyated diazoketo compounds (for details, see Supporting Information).

To assess hydride transfer in the formation of dienes **9** from vinydiazoesters **8** deuterium-labeled **8a-d_1** and **8a-d_3** were prepared and subjected to treatment with Tf$_2$NH. Compound **9a-d_1** was the sole diene product formed from **8a-d_1**, and its deuterium resided only at the γ-position, suggesting that 1,3-

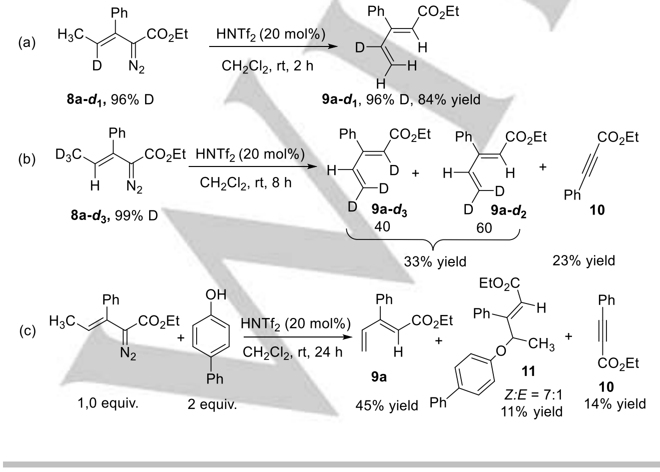
10.1002/anie.202004328

hydride transfer is not involved in the formation of this product (Scheme 6a). Treatment of **8a-*d*₃** under the standard reaction conditions formed **9a-*d*₃**, confirming 1,4-deuterium transfer, but also formed **9a-*d*₂**, which in view of the outcome of reaction with **8a-*d*₁** is not consistent with 1,3-hydride transfer. Relative to the reaction with the undeuterated **8a**, that with **8a-*d*₃** underwent diene formation in much lower yield (33% vs, 84%), but a C-C bond cleavage product, ethyl 3-phenylpropiolate (**10**) was also isolated (Scheme 6b) in a yield comparable to those of **9a-*d*₃** and **9a-*d*₂**. Fragmentation products resulting in alkyne products from vinyl cation intermediates have been well documented,[19] but this is the first reported example that formally releases an alkyl cation.[20] In efforts to trap chemical intermediates, a variety of nucleophiles were added to the reaction mixture prior to treatment with Tf_2NH; as previously mentioned, no Friedel-Crafts product was formed in the reaction conducted in benzene, but in the presence of *p*-phenylphenol diene **9a**, alkyne cleavage product **10**, and the phenolic trapping product **11** were formed (Scheme 6c). Compound **11** is consistent with 1,3-hydride transfer or 1,2-hydride transfer following initial 1,4-hydride transfer from the vinyl cation. The ethyl ether of *p*-phenylphenol was detected by LC-MS, but only in a trace amount.

Scheme 5. Scope of the $HNTf_2$-promoted dedinitrogenation of γ-methyl substituted vinyldiazo compounds.[a]



[a] Reactions were performed by adding $HNTf_2$ (20 mol%) to **1** (0.3 mmol) in CH_2Cl_2 solvent (3 mL), unless otherwise noted; Isolated yield after chromatography. [b] 10 mol% catalyst loading. [c] Cleavage product *p*-$MeC_6H_4CCCO_2Et$ was obtained in 7% yield.



Scheme 6. 1,4-Hydride transfer and fragmentation determined from labelling experiment.

The vinyl cation pathway to diene and cleavage products is less certain than is that for Friedel-Crafts-type reactions. Deuterium isotope studies point to 1,4-hydride transfer as being the dominant route, but 1,3-hydride transfer or 1,4-hydride transfer to the homoallylic cation (**int-V**) with subsequent 1,2-hydride transfer to the allyl cation (**int-VI**) cannot be ruled out (Figure 2). Trapping of **int-VI** by a phenol demonstrates that this cationic intermediate is formed, even though the deuterium-labeling experiment suggests that this intermediate is not formed by direct 1,3-hydride transfer. The C-C bond cleavage reaction of the vinyl cation that forms ethyl propiolate (**10**) may or may not invole formation of an ethyl cation intermediate. Attempts to trap this cation or its triflimide[9b] were unsuccessful.

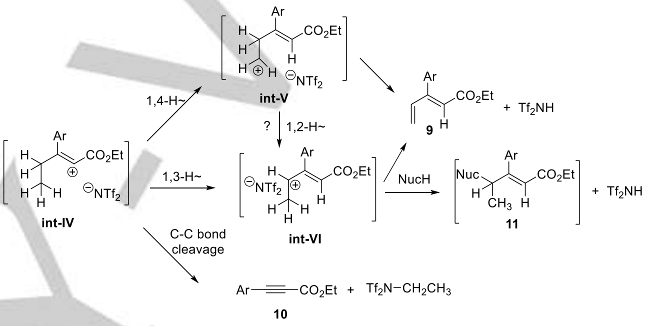


Figure 2. Proposed mechanism for dedinitrogenation reaction.

In summary, we have realized Friedel-Crafts-type coupling and dedinitrogenation reactions of vinyldiazo compounds *via* Brønsted acid catalysis. Vinyldiazo compounds are the precursors of α-diazo β-carbocations (vinyldiazonium ions) that, upon extrusion of dinitrogen, form highly reactive acyclic vinyl cations. These reactive intermediates were not trapped by nucleophiles and, instead, rearranged to allylic or homoallylic carbocationic species. With indoles as nucleophiles, vinyldiazonium ion intermediates are captured, delivering β-indole substituted diazo esters having an adjacent quaternary center in good yields. Loss of dinitrogen to the putative vinyl cation then enabled 1,3-hydride transfer to the more stable allyl cation that underwent Friedel-Crafts reaction with arenes to form α,β-unsaturated esters in good to high yields and selectivities. γ-Methyl-substituted vinyldiazo compounds also formed vinyl cations that underwent hydride transfer to reform the $HNTf_2$ catalyst without being trapped by an arene. These results demonstrate the intriguing reactivity of vinyldiazo compounds in Brønsted acid catalysis and also provide a fascinating methodology for the selective synthesis of trisubstituted α,β-unsaturated esters, β-indole substituted diazo esters, and dienes. Further studies are ongoing to explore the full scope of cation addition to the vinylogous position of vinyldiazo compounds that form vinyldiazonium ions.

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Keywords: trifluoromethanesulfonimide • vinyldiazo compounds• Friedel-Crafts coupling • dedinitrogenation • vinyl cation

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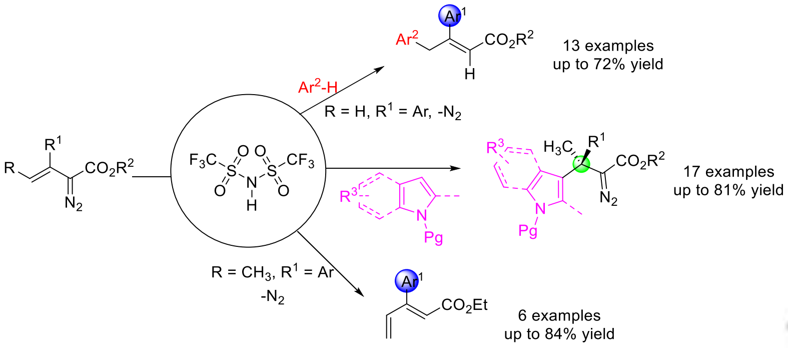
[20] Reassessment of results presented in Scheme 5 showed that the alkyne cleavage product was present in most reaction mixtures, albeit in small amounts, but in 7% yield from reaction with **9b**.

Entry for the Table of Contents

COMMUNICATION



Brønsted acid catalysis provides direct Friedel-Crafts-type coupling and dedinitrogenation reactions of vinyldiazo compounds. In this acid-catalyzed methodology, vinyldiazo compounds serve as the precursor of vinyldiazonium ions, vinyl, and high reactive allylic and homoallylic carbocation species. By choosing suitable nucleophilic reagents to capture these intermediates, both trisubstituted α,β-unsaturated esters, β-indole substituted diazo esters and dienes are obtained in good yields and selectivities.

H. F. Zheng, K. Y. Dong, D. Wherritt, H. Arman, M. P. Doyle

Page No. – Page No.

Brønsted Acid Catalyzed Friedel-Crafts-type Coupling and Dedinitrogenation Reactions of Vinyldiazo Compounds