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Construction of Diazo Compounds via Catalytic [3 + 2] Annulation of Vinyldiazoacetates and Their Synthetic Applications

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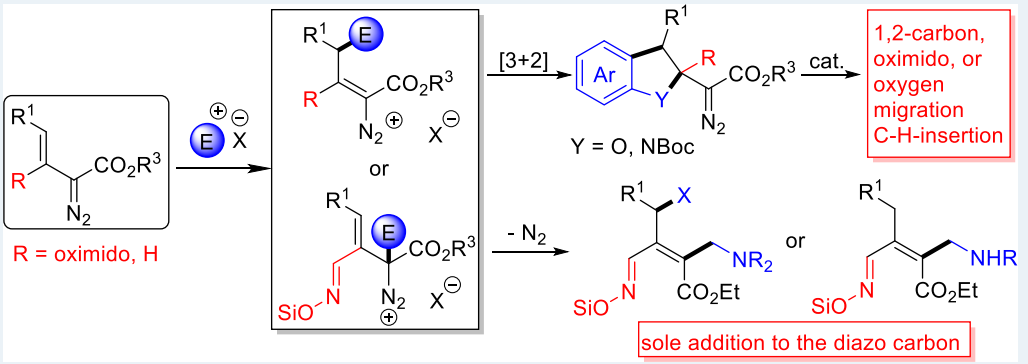

ABSTRACT: Highly selective formal [3 + 2]-cycloaddition of vinyldiazoacetates with quinone ketals and quinoneimine ketals has been accomplished at room temperature with catalytic amounts of the Brønsted acid triflimide, leading to highly functionalized diazoacetates in good yields. The vinyldiazonium ion generated by electrophilic addition to the vinylogous position of the reactant vinyldiazo compound is the key intermediate in this selective transformation. Both oximidovinyldiazoacetates and those with other vinyl substituents undergo cycloaddition reactions with quinone ketals whose products, after extended reaction times, undergo substrate-dependent 1,2-migration; catalysis by $Rh_2(OAc)_4$, $HNTf_2$, and $Sc(OTf)_3$ effects these 1,2-migrations to the same products. However, the products from $HNTf_2$-catalyzed reactions between quinoneimine and oximidovinyldiazoacetates undergo $Rh_2(OAc)_4$-catalyzed 1,3-C−H insertion. 1,3-Difunctionalization products are obtained for electrophilic reactions of Eschenmoser's salt with selected vinyldiazoacetates, but with α-dibenzylaminomethyl ether, 1,6-hydride transfer reactions are observed with oximidovinyldiazoacetates.

KEYWORDS: *Brønsted acid catalysis, vinyldiazo compounds, vinyldiazonium ions, cycloaddition, rearrangement*

INTRODUCTION

Vinyldiazo compounds prove to be versatile reactants for the synthesis of complex products. Their transition-metal-catalyzed reactions that form metal carbene intermediates provide access to a variety of natural products through cyclopropanation and C−H insertion,[1] as well as to diverse carbocyclic and heterocyclic compounds by intermolecular [3 + *n*]-cycloaddition.[2] Their reactions with electrophiles can occur either at the vinylogous position or at the diazo carbon. Electrophile addition at the vinylogous position produces either new diazo compounds with a quaternary carbon adjacent to the diazo carbon[3] or vinyl carbocations with the release of dinitrogen.[4] When electrophilic addition occurs at the diazo carbon, as in metal carbene formation or proton addition, subsequent nucleophilic reactions can occur at either the site of electrophilic addition[5] or at the vinylogous position.[6] The core feature of electrophilic addition that occurs at the vinylogous position is the formation of vinyldiazonium ions that are either captured by a reaction-generated nucleophile or lose dinitrogen to form vinyl cations. With the objective of retaining the diazo functional group, discovering suitable carbon electrophiles that can also generate a nucleophile to trap the vinyldiazonium ion is a challenge. We have previously reported (Scheme 1a) the use of quinone ketals, quinoneimine ketals, and Eschenmoser's salt as suitable electrophiles or their precursors in reactions with 3-aryl- or 3-methyl-2-diazo-3-butenoates to restrain the loss of dinitrogen by making available a nucleophile/base to provide alternative strategies for the preparation of structurally complex diazo-containing compounds,[7] and this concept is further expanded by the results reported in this manuscript.

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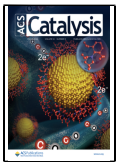

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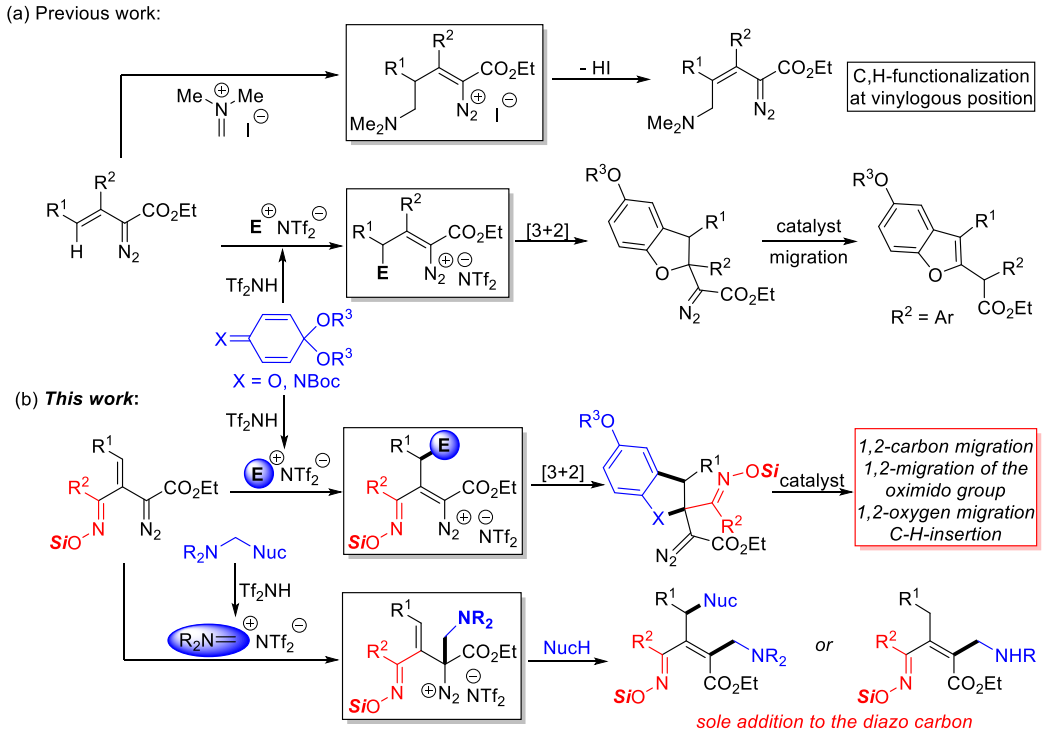
Scheme 1. Catalytic Transformations of Vinyldiazo Compounds



We have also recently reported the synthesis of a new class of vinyldiazoacetates, having an oximido group at the β-position, that provides enormous skeletal and functional group flexibility.[8] These diazo compounds are produced in very high yields by mild base-catalyzed Dimroth-type rearrangement of 1,2,3-triazine 1-oxides.[9] Since all prior investigations involving carbon electrophile addition to vinyldiazoacetates have used β-aryl- or β-alkylvinyldiazoacetates, would oximidovinyldiazoacetates with their basic oxime functionality undergo similar transformations (Scheme 1b)? We now report that except for iminium salts, electrophilic addition to vinyldiazoacetates provides a convenient methodology for the synthesis of structurally complex diazo compounds that offer directed syntheses of new heterocyclic compounds via intriguing and surprising subsequent reactions.

RESULTS AND DISCUSSION

When treated with catalytic amounts of triflimide at room temperature, quinone ketals undergo 1,3-difunctionalization ([3 + 2]-cycloaddition) across the C=C of β-aryl- and β-alkyl-vinyldiazoacetates to form benzofuranyl-diazoacetates in moderate to good yields with high diastereocontrol (Scheme 1a).[5] Under the same conditions, oximidovinyldiazoacetates **1** undergo the same transformation with ketals of quinine **2a**, producing **3** in moderate to good yields and high diastereocontrol (Scheme 2). Their stereochemistry was confirmed by NOE experiments. Apparently, the oximido functional group has no influence on this transformation nor do R^1 and R^2 substituents, various esters including one with a styryl double bond, or using triisopropylsilyl (TIPS) instead of *tert*-butyldimethylsilyl (TBS). Quinone imine ketal **2b** also gave the corresponding cycloaddition products **3o** and **3p** in good yields but with low diastereocontrol in the case of **3o** at room temperature that showed very high diastereoselectivity when the same reaction was performed at 0 °C.

Vinyldiazo compounds other than those that are substituted at the β-position also undergo this proton-catalyzed cycloaddition. Methyl styryl diazoacetate,[4,10] for example, reacts with quinone ketal **2a** to produce the corresponding benzodihydrofuran **5a** in excellent yield and diastereocontrol, and benzodihydropyrrole **5b** is also produced from its reaction with quinoneimine ketal **2b**, albeit in somewhat lower yield but high diastereocontrol (Scheme 3). Surprisingly, the ethyl-vinyldiazo ester analogue of the styryl diazoacetate, **7**, as well as the unsubstituted benzyl 2-diazo-3-butenoate, **10**, did not produce their corresponding α-diazoacetates (**8** and **11a**) and, instead, formed benzopyran **9** or benzofuran **12** in moderate to good yields. For these processes, conversion of the initially formed α-diazoacetate to their corresponding benzopyran or benzofuran by proton-induced diazonium ion formation (**9′** and **12′**) and subsequent 1,2-oxygen migration or 1,2-hydrogen migration explain the reaction outcomes. However, performing these reactions at a lower temperature resulted in the formation of the precursor α-diazoacetates (**8** and **11a**). Also, extending the reaction time for the reaction with styryl diazoacetate (**4**) resulted in the conversion of **5a** to its corresponding benzopyran **6** via **6′** and subsequent 1,2-oxygen migration. As expected, the imido analogue **5b** was more stable to proton-induced denitrogenation and rearrangement. Treatment of benzyl 2-diazo-3-butenoate (**10**) with the less reactive quinoneimine ketal **2b** resulted in the formation of benzodihydropyrrole **11b** with the retention of the diazo functionality. What is particularly notable about these transformations is the ability to control the individual steps of cycloaddition and the subsequent denitrogenative rearrangement.

To further understand the denitrogenative rearrangement process, we treated representative α-diazoacetate products from the [2 + 3]-cycloaddition between oximidovinyldiazoacetates and quinone ketal **2a** with dedinitrogenation reagents,

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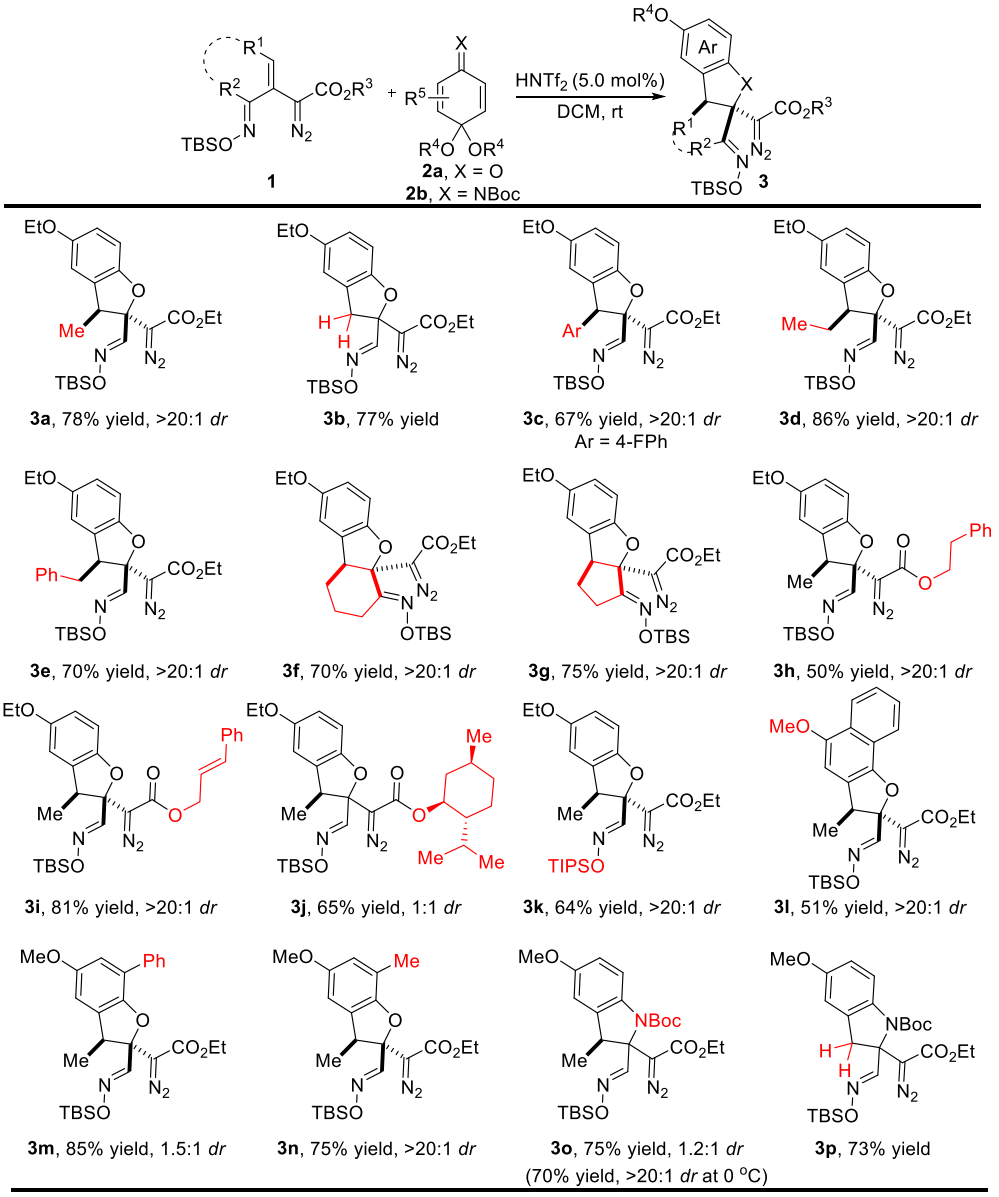
Scheme 2. Catalytic [3 + 2]-Cycloaddition Reaction of Oximidovinyldiazo Compounds[a]



[a]Reaction conditions: to vinyldiazo compounds **1** (0.1 mmol), quinone or quinone imine ketals **2** (0.2 mmol, 2.0 equiv), and 4 Å MS (50 mg) in anhydrous DCM (1.0 mL) was added a solution of $HNTf_2$ (0.9 mg, 5 mol %) in anhydrous DCM (1.0 mL) via a syringe pump over 2 h at room temperature.

especially dirhodium tetraacetate. Because the carbon adjacent to the diazo functionality is tertiary with possible oximido, oxygen, or carbon migration to the electrophilic center, all three migratory outcomes are possible.[11] With free rotation around the C−C bond to the electrophilic carbon, rearrangement is dependent upon migratory aptitude as well as on the special positioning of the migrating group relative to the electrophilic center.[12] Not surprisingly, these reactions occurred under mild conditions, but subtle structural changes in the reactants resulted in dramatic changes in 1,2-migration (Scheme 4). For example, despite the enormous difference in the probable mechanisms of reactions with $Rh_2(OAc)_4$ (metal carbene intermediate), $Sc(OTf)_3$ (coordination with the diazo dinitrogen), and $HNTf_2$ (diazonium ion intermediate), their reactions at room temperature with the methyl-substituted **3a** gave the same products in nearly the same molar ratios. 1,2-Carbon migration yielding **13a** was dominant, but 1,2-migration of the oximido group yielding **14a** was competitive. Only carbon and oximido group migrations produce oxonium ion intermediates in these reactions, and oximido group migration is rare[13] and has not been previously reported in similar electrophilic reactions. Lowering the temperature of the $Rh_2(OAc)_4$-catalyzed reaction did cause a small change in the product ratio. Contrast this to the same reactions with **3b** in which, once again, the product ratios from $Rh_2(OAc)_4$- and $HNTf_2$-catalyzed reactions were nearly identical at room temperature, but the reaction catalyzed by $Sc(OTf)_3$ at the same temperature gave **14b** without evidence of **13b**. However, when these reactions were performed at 0 °C with $Rh_2(OAc)_4$ and $HNTf_2$ catalysis, **14b** was similarly dominant, suggesting an important role of the conformational factors in these migrations.

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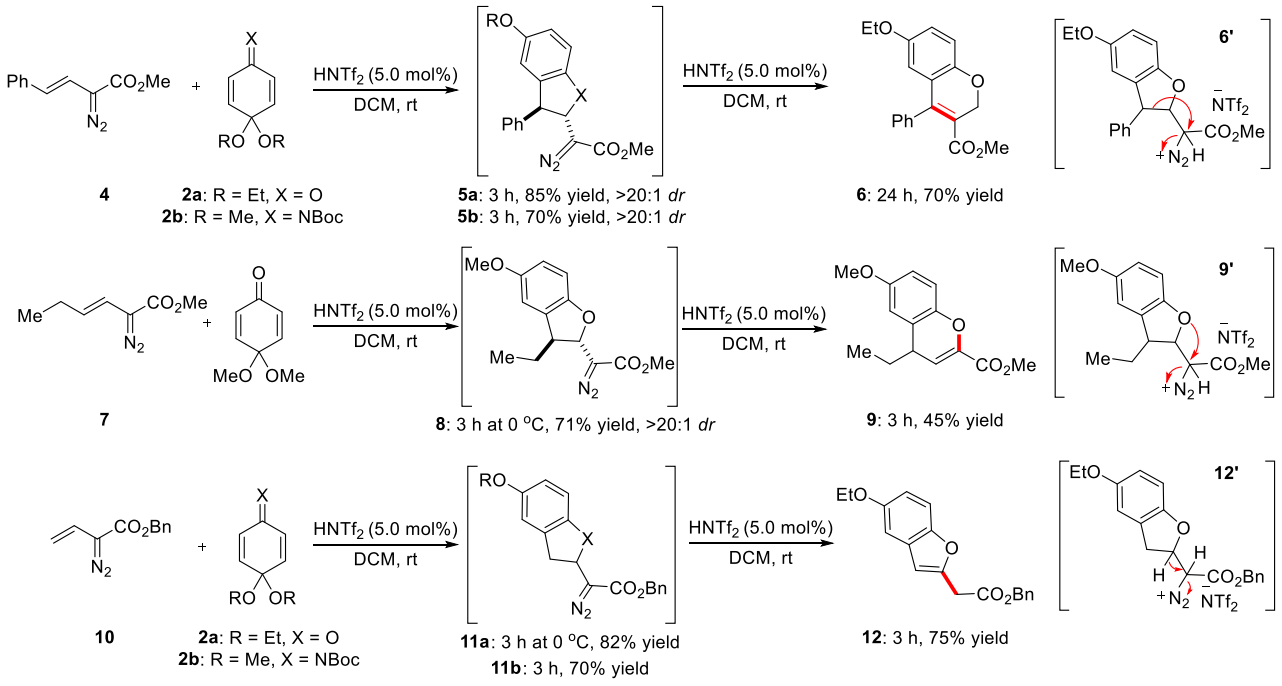
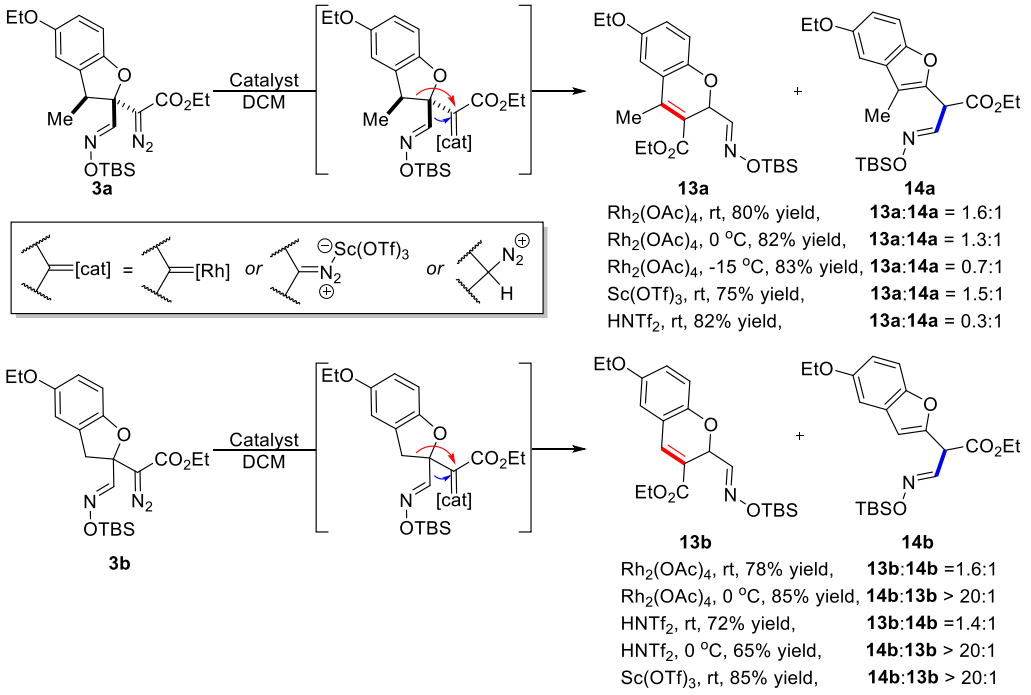
Scheme 3. Catalytic [3 + 2]-Cycloaddition Reaction of Other Vinyldiazo Compounds



Scheme 4. Selectivity in Catalytic Migration Reactions of Benzohydrofuranyl-α-diazoacetates



However, high migration selectivity was the outcome of other similarly constructed benzohydrofuranyl-α-diazoacetates (Scheme 5). Surprisingly, the 4-fluorophenyl analogue **3c** and both ring-fused **3f** and **3g** underwent only 1,2-oxygen rearrangement without evidence of either oximidyl or carbon rearrangement. In yet another migration reversal, the styryl diazoacetate-derived **5a** underwent only 1,2-carbon migration in the $Rh_2(OAc)_4$-catalyzed reaction. The molecular connectivity of these products was assigned by NMR analyses that included 2D-spectroscopic methods. In contrast to these results, β-aryl-β-benzodihydrofuranyl-α-diazoacetates underwent exclusive denitrogenation/aryl migration in reactions catalyzed by $Sc(OTf)_3$.[7]

To our great surprise, however, treatment of the crowded benzopyran-substituted α-diazoacetate **3o** with dirhodium tetraacetate not only formed the 1,2-carbon migration product **16a** but also produced the fused cyclopropane product **17a** that would arise from C−H-insertion into the sp^3-hybridized C−H bond on the carbon adjacent to the methyl group (eq 1), and the same product ratio was obtained at a lower temperature. Although such 1,3-C−H insertion reactions are known for free carbenes,[14] they are very rare in metal carbene

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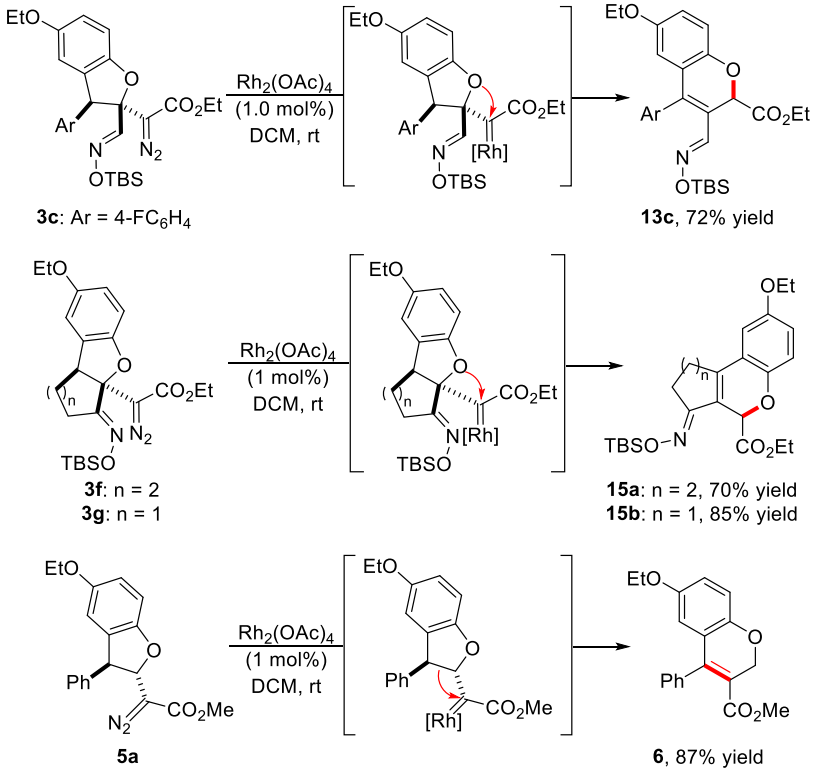
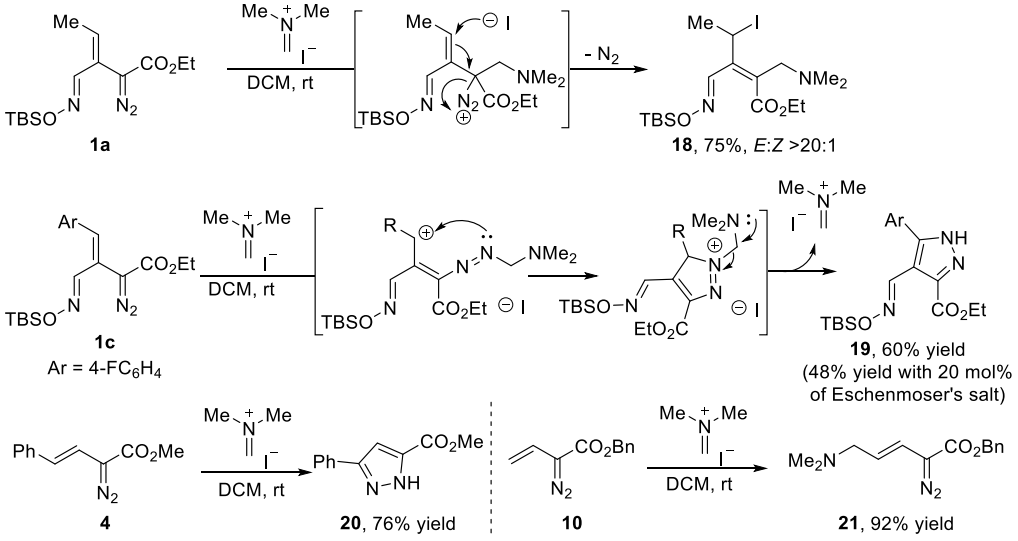
Scheme 5. High Selectivity in $Rh_2(OAc)_4$-Catalyzed Reactions of Representative Benzohydrofuranyl-α-diazoacetates



Scheme 6. Catalytic Functionalization of Vinyldiazo Compounds with Eschenmoser's Salt



reactions.[15] In the case of **3o**, the formation of **17a** stands in direct contrast with its benzofuran analogue **3a**, which exhibits no evidence for 1,3-cyclopropanation in its $Rh_2(OAc)_4$-catalyzed reaction (Scheme 4). The presence of bulky Boc attachment to nitrogen appears to be the governing factor. Indeed, performing the same reaction with the benzopyrrole analogue of **3p** without the pendant methyl group produced the same products but with a different product ratio (eq 2). And a lower temperature was beneficial for generation of the C−H-insertion product.

Another measure of reactivity for vinyldiazo compounds is the site selectivity in their reactions with electrophiles. Vinylogous electrophilic addition retains the diazo functional group, whereas addition to the diazo carbon ordinarily results in the extrusion of dinitrogen and the formation of an allylic cation. The electrophiles formed from quinone ketals and quinoneimine ketals, as well as Eschenmoser's salt, only underwent vinylogous addition with vinyldiazoacetates, 3-aryl-2-diazo-3-butenoates, and other similarly substituted vinyldiazoacetates.[7] Triflimide addition of a proton to these vinyldiazoacetates also occurs by the same pathway.[3b] Thus, we were surprised to discover that treatment of oximidovinyldiazoacetate **1a** with Eschenmoser's salt underwent sole addition to the diazo carbon resulting in the formation of the iodide-substituted product **18** in good yield (Scheme 6). In contrast, reaction of **1c** with the Eschenmoser salt resulted in

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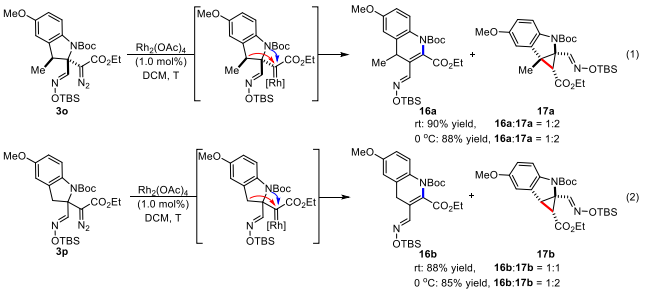
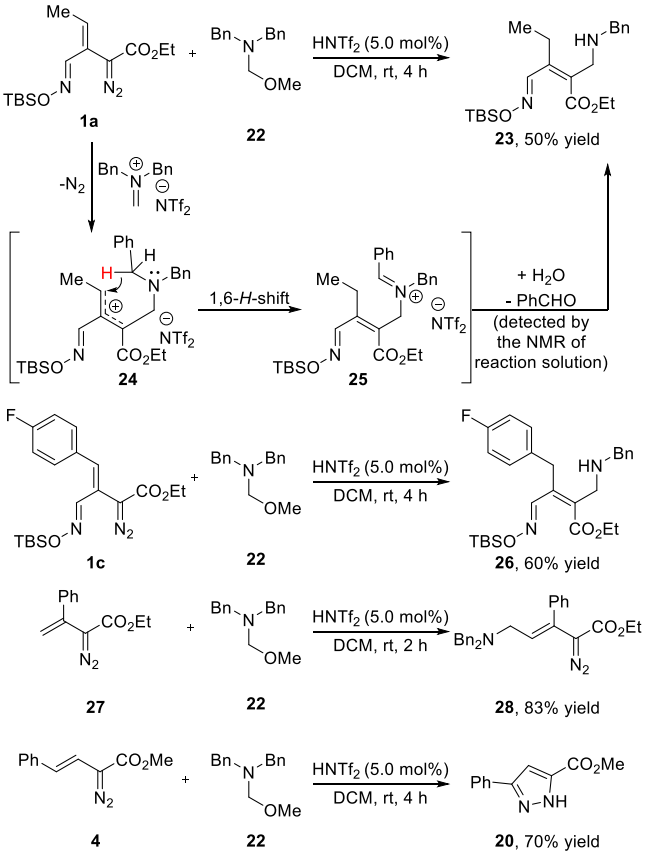
the product from intramolecular vinyldiazoacetate ring closure[16] to pyrazole **19**. Indeed, when this same reaction was performed with a catalytic amount of the Eschenmoser salt, pyrazole **19** was the sole product (48% yield); and the same outcome (**20**) occurred in the reaction with styryl diazoacetate **4**. These results stand in direct contrast with the outcome of the same reaction performed with ethyl 3-methyl-2-diazo-3-butenoate **10** in which the product was that from addition of Eschenmoser's salt to the vinylogous position of the vinyldiazoacetate (**10**) followed by proton loss from the resulting vinyldiazonium ion.[7]



Another way to form similar iminium ions is by acid-promoted demethoxylation of tertiary α-methoxymethylamines,[17] and we selected commercially available α-dibenzylaminomethyl ether **22** for these experiments. Treatment of vinyldiazoacetates with iminium ions formed in this way was expected to produce products that were similar to those from their reactions with Eschenmoser's salt (Scheme 6). However, reaction of oximidovinyldiazoacetate **1a** with **22** that was treated with a catalytic amount of triflimide at room temperature (Scheme 7) gave an addition product (**23**) that could be attributed to iminium ion addition to the diazo carbon, but its structure implied rearrangement and the loss of a benzyl group. Thorough analyses found benzaldehyde (detected by the NMR of reaction solution) as a byproduct in a 1:1 **23**:benzaldehyde ratio and a molecular connectivity that suggested a mechanistic pathway involving 1,6-hydride transfer and hydrolytic formation of benzaldehyde from the intermediate iminium ion **25**. Thus, the overall process involves electrophilic addition of the iminium ion at the diazo carbon, dinitrogen loss to produce an allyl cation **24**, and then an intramolecular 1,6-hydride transfer to **25**, which is a relatively common transformation when the outcome is formation of an iminium ion.[18] Extension of this procedure to oximidovinyldiazoacetate **1c** gave the same outcome with **26** which was obtained in 60% isolated yield. However, reaction with ethyl 3-phenyl-2-diazo-3-butenoate **27**, like its reaction with Eschenmoser's salt,[7] formed the product from vinylogous addition (**28**) with subsequent deprotonation; and its styryl diazoacetate isomer (**4**) underwent intramolecular vinyldiazoacetate ring closure[15] to pyrazole **20**, identical with its outcome by treatment with Eschenmoser's salt (Scheme 6).

Vinylogous electrophilic addition to vinyldiazoacetates that occur in preference to addition at the diazo carbon are rare compared with their nucleophilic counterparts that characterize transition-metal-catalyzed reactions that take place with metallovinylcarbenes.[19] The few examples of electrophilic addition show exclusive vinylogous addition to 3-substituted-2-diazo-3-butenoates (substituent = aryl and alkyl) and 2-diazo-3-butanoate,[7,20] and the same selectivity is obtained in oximidovinyldiazoacetate reactions with quinone ketals and quinoneimine ketals (Schemes 2 and 3). The addition of

Scheme 7. Catalytic Functionalization of Vinyldiazo Compounds with α-Aminomethyl Ether



iminium salts to the diazo carbon of oximidodiazoacetates contrasts with the "normal" vinylogous reactivity of vinyldiazoacetates, and a cause of this anomalous reactivity is the probable deactivation of the vinylogous position by the electron-withdrawing oxime functional group.

CONCLUSIONS

In summary, the reactions of electrophiles with vinyldiazoacetates occur by substrate-dependent addition to either the diazo carbon or its vinylogous position to produce a diversity of products. *p*-Quinone-derived electrophiles undergo 1,3-difunctionalization at the vinylogous position to give benzohydrofuranyl-diazoacetates that are subject to subsequent transformations due to electrophilic reagents but not those derived from quinones. Electrophilic catalysts that include those capable of forming metal carbenes, diazonium ions, or activation of the diazo carbon by Lewis acids effect 1,2-migration of benzohydrofuranyl-diazoacetates to give substrate-dependent products. However, benzopyrrole-substituted α-diazoacetates undergo $Rh_2(OAc)_4$-catalyzed 1,3-C−H insertion competitive with 1,2-carbon migration. These catalytic transformations provide access to a diversity of heterocyclic benzohydropyran compounds that are not readily accessible by other methods. With Eschenmoser's salt, which is less electrophilic than those derived from quinones, addition occurs not only at the diazo carbon with oximidovinyldiazoacetates but also at the vinylogous position with vinyldiazoacetates and catalytically activates the vinyldiazoacetates for intramolecular pyrazole formation. The iminium ion derived from α-dibenzylaminomethyl ether also underwent

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electrophilic addition to the diazo carbon, but a subsequent 1,6-hydride transfer occurred. In contrast, electrophilic addition to ethyl 3-phenyl-2-diazo-3-butenoate occurred at the vinylogous position. The overall results describe vinyldiazoacetates as unique in electrophilic transformations, capable of a diversity of selective chemical processes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.4c01291.

Experimental procedures and spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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