Silver Catalysis

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Catalyst-Dependent Chemoselective Formal Insertion of Diazo Compounds into C–C or C–H Bonds of 1,3-Dicarbonyl Compounds

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Abstract: A catalyst-dependent chemoselective one-carbon insertion of diazo compounds into the C–C or C–H bonds of 1,3-dicarbonyl species is reported. In the presence of silver(I) triflate, diazo insertion into the C(=O)–C bond of the 1,3dicarbonyl substrate leads to a 1,4-dicarbonyl product containing an all-carbon α -quaternary center. This reaction constitutes the first example of an insertion of diazo-derived carbenoids into acyclic C–C bonds. When instead scandium-(III) triflate was applied as the catalyst, the reaction pathway switched to formal C–H insertion, affording 2-alkylated 1,3dicarbonyl products. Different reaction pathways are proposed to account for this powerful catalyst-dependent chemoselectivity.

he construction of all-carbon quaternary centers by onecarbon insertions into C-C bonds is a formidable challenge, not only because of the difficulty of achieving the selective cleavage of inert C-C bonds,^[1] but also because of the subsequent formation of a congested quaternary carbon center.^[2] Progress in this field has been especially limited with acyclic systems,^[3] where insertions of diazo compounds into carbonyl compounds represent one approach to construct quaternary carbon centers.^[4] In such processes, the diazo compound invariably acts as an ambiphilic species, undergoing a sequential nucleophilic addition/1,2-rearrangement cascade.^[5] Whereas diazo compounds have also been widely explored as a source of carbenoids in transition-metal catalysis,^[6] the insertion of diazo-derived metal carbenoids into acyclic C-C bonds is unknown.^[7] To the best of our knowledge, only one report by Wang and co-workers has

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described a formal insertion of rhodium carbenoids derived from diazo compounds into the C–C bonds of strained benzocyclobutenols to form quaternary carbon centers through sequential C–C bond cleavage, carbene migratory insertion, and intramolecular aldol reaction.^[8]

We targeted a new method to achieve the insertion of diazo-derived carbenoids into acyclic C–C bonds.^[9] Based on achievements in the silver-catalyzed activation of diazo compounds by our group^[10] and others,^[11] we questioned whether inexpensive silver catalysts could be used to mediate C–C insertion. Although coinage metals have been extensively exploited in the alkylation of C(sp)–H,^[12] C(sp²)–H,^[13] and C(sp³)–H^[14] bonds with diazo compounds^[15] (e.g., Shi's report on an alkylation reaction; Figure 1a),^[16a] equivalent C–C insertions are unknown. Herein, we describe the realization of this process, which offers a new strategy to install all-carbon quaternary centers in acyclic systems.^[3c] In addition, the reaction pathway can be altered so that either C–C or C–H insertion occurs depending on the choice of catalyst (Figure 1b).^[17]

a) Shi's report

$$\frac{N_2}{Ph + CO_2Me} + R^1 + \frac{Q}{R^3} + \frac{(Au) cat.}{Ref. [16a]} + R^1 + \frac{Q}{R^3} + CO_2Me$$

b) This work
$$R^3 + \frac{Q}{R^1 + R^2} + \frac{(Ag) cat.}{C-C \text{ insertion}} + \frac{R^3 + R^4}{R^4} + \frac{(Sc) cat.}{C-H \text{ insertion}} + \frac{Q}{R^1 + R^2} + \frac{R^4}{R^2 + R^4}$$

Figure 1. Insertions of diazo compounds into 1,3-dicarbonyl species.

Initial studies revealed that the use of silver(I) triflate (10 mol%) as the catalyst in CH_2Cl_2 at 40°C exclusively afforded the C–C insertion product **3a** in 89% yield (Figure 2).^[18] When we performed the reaction in the



Figure 2. Initial results on the gold- and silver-catalyzed insertion of diazo compounds into 1,3-dicarbonyl species.

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presence of a gold catalyst,^[16a] **3a** and **4a** were obtained in 50% and 28% yield, respectively. While the reason for the generation of this mixture is unclear, it highlights the challenge of achieving selective C(=O)-C insertion over competing $C-H^{[16]}$ and $O-H^{[19]}$ insertions; complete selectivity for C-C insertion of diazo-derived carbenoids into 1,3-dicarbonyl species, as observed with AgOTf as the catalyst, has not been reported previously.

The scope of this silver-catalyzed chemoselective C(=O)-C insertion reaction was investigated next (Scheme 1). A variety of aryl diazoacetates, bearing either electron-poor (with F, Cl, Br, CO₂Me, or CF₃ substituents) or electron-rich (OMe, CH₃, *t*-Bu) arenes, were successfully converted into the desired C-C insertion products **3a**-**3k** in good to excellent yields. Aside from methyl and ethyl esters, isopropyl (**11**), benzyl (**1m**), allyl (**1n**), and 3-hexenyl (**1o**) phenyldiazoacetates were also suitable substrates, affording the corresponding products **3l**-**3o** in 75–96% yield. 2-Naphthyl- (**1p**), 2-thienyl- (**1q**), and 3-indolyl-substituted (**1r**) diazoacetates also proved to be suitable reaction partners, and the



Scheme 1. Scope of the C(=O)-C insertion. Reaction conditions: 1 (0.3 mmol) in CH₂Cl₂ (5.0 mL) was added dropwise (1 h) to a mixture of AgOTf (10 mol%) and **2** (0.45 mmol) in CH₂Cl₂ (1.0 mL) at 40 °C. Yields of isolated products are given.

connectivity of **3r** was confirmed by single-crystal X-ray analysis.^[29] The present method was not restricted to α -diazoesters, with diazophosphonates **1s** and **1t** also reacting efficiently to afford products 3s and 3t, featuring a phosphorus-substituted α-quaternary center.^[20] Relatively non-stabilized diazo compounds, such as (1-diazo-2,2,2-trifluoroethyl)benzene (1u), the sterically hindered substrate diphenyldiazomethane (1v), and tricyclic 9-diazo-9*H*-fluorene (1w), were also compatible with the reaction conditions, delivering 3u-3w in 45–77% yield. A variety of symmetric 1,3-dicarbonyl substrates could be employed, including heteroaryl diketones, affording the expected 1,4-dicarbonyls 3aa-3af in good yields upon reaction with 1e. With an unsymmetric diaryl ketone, a 2:1 mixture of the isomers 3ag and 3ag' was obtained in 82% yield, illustrating the moderate electronic influence over the position of formal C-C insertion, while phenyl methyl 1,3diketone delivered 3ah exclusively in 58% yield as the reaction occurred selectively at the C(=O)-C bond next to the alkyl ketone. These two observations provided early insight into factors affecting the mechanism of the insertion process

Achieving catalyst control over the site of reactions such as insertion processes is an attractive goal.^[17] To our delight, we found that a switch from C(=O)-C insertion to C-H insertion into the 1,3-dicarbonyl species could be accomplished by employing $Sc(OTf)_3$ as the catalyst instead of AgOTf; at 80°C, complete selectivity for the C-H insertion was observed for substrate 1a and diketone 2a (to give 4a in 80% yield; Scheme 2).^[18,21] The scope of this complementary procedure proved to be equally as broad as that of the silvercatalyzed process, with the reactions of various ethyl aryl diazoacetates, bearing either electron-withdrawing or electron-donating groups, affording the C-H insertion products 4b-4j in good to excellent yields. The structure of compound 4c was unambiguously assigned by X-ray analysis.^[29] Isopropyl, benzyl, and allyl phenyldiazoacetate were also productive substrates, giving the expected products 4k-4m in good vields. 2-Naphthyl ethyl diazoacetate and cyclic 4-diazoisochroman-3-one also smoothly underwent selective C-H insertion to furnish 4n and 4o in 80% and 65% yield, respectively. A diazophosphonate again proved to be a suitable substrate, affording 1,3-diketone 4p in 52% yield. Excitingly, non-stabilized diazo compounds such as diphenyl, aryl, and alkenyl diazomethanes were accommodated, giving the products 4r-4v in 48-76% yield. Variation of the 1,3dicarbonyl compound in this scandium-catalyzed insertion was evaluated with ethyl phenyldiazoacetate and ethyl 4-methoxyphenyldiazoacetate. Pleasingly, the reaction proceeded smoothly irrespective of the electronic character of the diaryl dicarbonyl compound: Electron-donating and -withdrawing groups (at various positions of the aryl rings) and a dithiophene substrate all afforded the C-H insertion products in excellent yields (4aa-4ag). An alkyl 1,3-diketone and an aryl \beta-ketoester were also tested as substrates, and afforded the expected products **4ah** and **4ai** in 68% and 42% vield, respectively.

The reaction of methyl phenyldiazoacetate and 1,3-cyclohexanedione using either AgOTf or $Sc(OTf)_3$ as the catalyst offered insight into the mechanisms of these different

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Scheme 2. Scope of the C⁻H insertion. Reaction conditions: 1 (0.6 mmol) in DCE (5.0 mL) was added dropwise (1 h) to a mixture of 4 Å M.S. (40 mg), Sc(OTf)₃ (30 mol%), and **2** (0.3 mmol) in DCE (1.0 mL) at 80 °C. Yields of isolated products are given. DCE = 1,2dichloroethane, M.S. = molecular sieves.

insertion processes (Scheme 3). To our surprise, both catalysts exclusively furnished the O–H insertion product **5c** in 80% and 54% yield, respectively, without formation of the anticipated C(=O)–C or C–H insertion products **5a** and **5b**. We considered that **5c** might arise from coordination of the enol form of the cyclic 1,3-diketone to the metal ion (or to a metal carbenoid), subsequently generating the formal O–H insertion product. 1,3-Cyclohexanedione differs from the previous substrates in only being able to form a *trans* enol,^[22] which may suggest that the formation of a *cis* enol, potentially as a bidentate complex with the metal, is critical in mediating





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the C(=O)–C and C–H insertion reactions of acyclic 1,3dicarbonyl substrates.

On the basis of these results and related precedents,^[7,23] a plausible mechanism for the chemoselective one-carbon insertion of diazo compounds into acyclic 1,3-dicarbonyl species is proposed (Scheme 4). In the case of the silver-



Scheme 4. Proposed reaction mechanisms for the silver-catalyzed C–C and the scandium-catalyzed C–H insertions.

catalyzed C(=O)-C insertion, 1,3-diketone 2 is first converted by AgOTf into silver enolate A, which engages with diazo compound 1 to give the electrophilic silver carbenoid B following loss of molecular nitrogen. The cyclopropanation of **B** leads to intermediate C,^[24] which then undergoes a retroaldol fragmentation to afford intermediate D.^[25] Upon protonation by HOTf, D releases the 1,4-diketone product 3, with concomitant regeneration of the silver catalyst. In contrast to existing catalytic methods for the insertion of nucleophilic diazo compounds into ketones,^[4] the transient formation of an electrophilic silver carbenoid (B) and the subsequent cyclopropanation would represent a novel mode of carbenoid reactivity. Notably, the formation of product 3ah (Scheme 1) would be consistent with such a mechanism, where cyclopropanation occurs at the double bond of the predominant enol form (i.e., that of the methyl ketone), rather than a pathway that relies on migrating group ability, in which migration of the C2 carbon atom would likely be disfavored.

In the complementary scandium-catalyzed C–H insertion, protonation of the diazo compound **1** by HOTf could yield the diazonium ion **B'**, which displays carbocation-like reactivity,^[23] undergoing facile nucleophilic attack by the scandium enolate **A'** to give complex **C'**. The C–H insertion product **4** is then released, with regeneration of Sc(OTf)₃. In the absence of this chelate **A'** (Scheme 4), direct reaction on the more reactive enolate oxygen atom may instead by possible (to give **5c**). The divergent reactivity of the diazo compounds under different modes of catalysis is therefore rationalized by the putative formation of an electrophilic silver carbenoid species in the presence of AgOTf, whereas in the presence of Sc(OTf)₃, the diazo compound behaves as a carbocation source. To test the robustness of this chemoselective one-carbon C–C insertion, a multigram-scale experiment was performed (Scheme 5). When 10 mmol of **1e** and **2a** were subjected to



Scheme 5. Multigram synthesis and further transformations. Reagents and conditions: a) HCl·1,4-dioxane, 80°C, 30 h; b) NH₄OAc/AcOH, 120°C, 36 h; c) TsOH (50 mol%), toluene, 110°C, 8 h; d) 20 wt% NaOH, 120°C, 30 h; e) N₂H₄·H₂O/EtOH, reflux, 12 h.

the standard silver-catalyzed reaction conditions, product **3e** was isolated in 79% yield (3.1 g). The synthetic versatility of 1,4-diketone **3e** was then explored in an array of derivatizations. Under strongly acidic conditions (path a), **3e** rearranged to give tricarbonyl compound **4b** (84%),^[26] whereas under Paal–Knorr conditions, **3e** was transformed into either the tetrasubstituted pyrrole **6a** (path b, 62%) or 2,3,5-triphenylfuran **6b** (path c, 70%), which are both important motifs in bioactive natural products, pharmaceuticals, and photoelectric materials.^[27] Alternatively, treatment of **3e** with base led to γ -oxo acid **6c** (path d), a key precursor for the synthesis of bioactive pyridazine derivatives,^[28] while reaction with hydrazine hydrate (path e) afforded the 4,6-diarylpyridazin-3(2*H*)-one **6d** in 85% yield.

In summary, we have developed a catalyst-controlled chemoselective insertion of diazo compounds into acyclic 1,3dicarbonyl compounds. In the presence of AgOTf, a onecarbon insertion of diazo-derived carbenoids into acyclic C-C bonds was achieved, affording 1,4-dicarbonyl products with a quaternary α -carbon atom. In contrast, the use of Sc(OTf)₃ as the catalyst led to a switch in chemoselectivity, now effecting a formal C-H insertion and leading to products of 1,3-dicarbonyl alkylation. The divergent reactivity of the diazo compounds was ascribed to the different catalytic activities of the Ag and Sc catalysts. Taken together, this work opens a new avenue for exploring rarely reported one-carbon insertion reactions into acyclic C-C bonds. Moreover, it demonstrates the great potential of such metal catalysts in controlling the activation mode of diazo compounds. Investigations into the development of asymmetric variants of these divergent catalytic processes are underway.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: 1,3-dicarbonyl compounds · C-C insertion · C-H insertion · diazo compounds · silver catalysis

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Catalyst-Dependent Chemoselective Formal Insertion of Diazo Compounds into C-C or C-H Bonds of 1,3-Dicarbonyl Compounds



Catalyst control: The catalyst-dependent chemoselective insertion of diazo compounds into 1,3-dicarbonyl species is reported. In the presence of AgOTf, the diazo compounds selectively insert into the C(=O)-C bond, affording 1,4-dicarbonyl products with an all-carbon α quaternary center. In contrast, in the presence of Sc(OTf)₃, C-H insertion results in α -C-H alkylation products.

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