C–C Coupling Reactions

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Copper(I)-Catalyzed Chemoselective Coupling of Cyclopropanols with Diazoesters: Ring-Opening C–C Bond Formations

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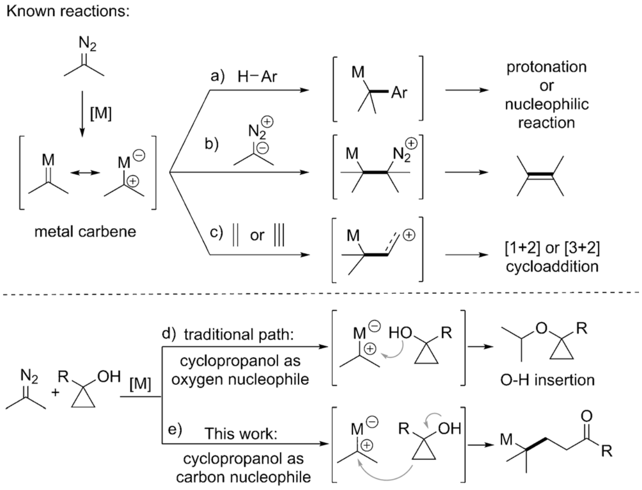
Abstract: *Reported herein is an exceptional chemoselective ring-opening/C(sp^3)–C(sp^3) bond formation in the copper(I)-catalyzed reaction of cyclopropanols with diazo esters. The conventional O–H insertion product is essentially suppressed by judicious choice of reaction conditions. DFT calculations provide insights into the reaction mechanism and the rationale for this unusual chemoselectivity.*

Transition-metal-catalyzed carbene-transfer reactions have emerged as powerful tools for preparing various functionalized organic compounds. In particular, generated from diazo substrates and late-transition-metal catalysts (e.g. Rh^{II} or Cu^{I}), the electrophilic metal-carbene species react with a range of nucleophiles, especially heteroatom-based reagents. These transformations provide efficient methods for constructing carbon–heteroatom bonds.[1]

In contrast, despite the recent development of elegant catalytic C–H functionalization methods by metal-carbene insertion, few coupling reactions between a metal carbene species and a carbon nucleophile have been reported, and offer an important means to form C–C single or double bonds. The most commonly explored carbon nucleophiles are electron-rich aromatic and heterocyclic compounds (Scheme 1a). In this type of transformation, benzyl metal species are generated, and subsequent protonation[2a–f] or nucleophilic substitution[2g,h] leads to the construction of C(sp^2)–C(sp^3) bonds. The diazo compound itself is also an efficient nucleophile (Scheme 1b). These formal dimerizations, which have long been considered as useless side reactions, have been explored for the synthesis of alkenes[3a–c] and fused rings[3d] recently. In addition, alkenes and alkynes have also been considered nucleophilic reagents in some cases (Scheme 1c). The generated intermediates can undergo [1+2] reactions[4a] or [3+2] reactions.[4b]



Scheme 1. Reaction of nucleophiles with metal carbenes derived from diazo compounds.

Although significant progress has been made, the scope with respect to the carbon nucleophiles which can be employed to couple with diazo compounds remains to be explored. In connection to our interests in both carbene chemistry and cyclopropanes,[5] we have chosen to explore cyclopropanols as carbon nucleophiles in transition-metal-catalyzed carbene-transfer reactions, considering the fact that ring-strain relief should provide an additional driving force for the transformation.[6] While cyclopropanols have been previously employed as carbon nucleophiles in reactions with protonic acids,[7] hypervalent halogen compounds,[8] or metal salts,[9] an obvious reaction between cyclopropanols and diazo compounds is nevertheless the metal-catalyzed O–H insertion with the carbene generated (Scheme 1d).[10] To address this unmet challenge, herein we describe our development of a copper(I)-catalyzed coupling between cyclopropanols and diazo compounds (Scheme 1e).[11,12] The unusual chemoselectivity observed in this transformation is rationalized by the DFT calculations.

Initially, phenylethyl cyclopropanol (**1a**) and the diazo ester **2a** were employed as the model substrates with [$Rh_2(OAc)_4$] as the catalyst (Table 1, entry 1). As expected, only the O–H insertion product **3a** was obtained in 64% yield. After testing a series of other metal catalysts, including Rh^{I}, Fe^{II}, Ag^{I}, and Cu^{II} salts, no improvement was observed (entries 2–5). Surprisingly, the use of CuI as the catalyst gave 18% yield of the ring-opening/coupling product (entry 7) **4a**, whereas CuBr was not effective (entry 6). Upon examining the effect of solvents, MeCN was shown to significantly

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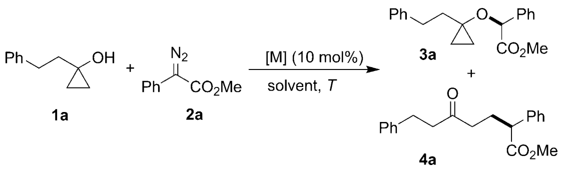
Table 1: Optimization of reaction conditions.[a]



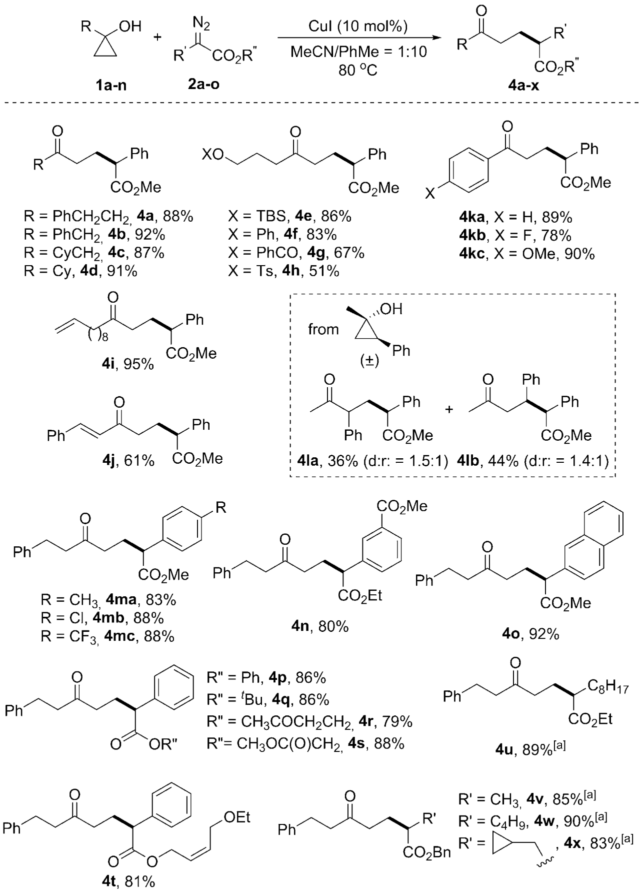
Entry	Cat. [M]	Solvent	T [°C]	**3a**, %	**4a**, %
1	$Rh_2(OAc)_4$	PhMe	60	64	<5
2	[Rh(COD)OH]	PhMe	60	<5	<5
3	$Fe(OAc)_2$	PhMe	60	<5	<5
4	$AgNO_3$	PhMe	60	18	<5
5	$CuBr_2$	PhMe	60	27	<5
6	CuBr	PhMe	60	18	<5
7	CuI	PhMe	60	24	18
8	CuI	MeCN	60	<5	38
9	CuI	1,4-dioxane	60	21	11
10	CuI	MeCN	70	6	47
11[c]	CuI	MeCN	70	<5	54
12[d]	CuI	MeCN	70	8	57
13[c]	CuI	MeCN/PhMe (1:10)	70	6	79
14[c]	CuI	MeCN/PhMe (1:10)	80	5	92

[a] Reaction conditions are as follows unless otherwise noted: **1a** (0.10 mmol), **2a** (0.10 mmol), and the catalyst (0.01 mmol) were stirred in 0.5 mL solvent at the indicated temperature for 2 h. [b] The yield was determined by ^1H NMR spectroscopy using $MeNO_2$ as the internal standard. [c] 1.5 equiv of **2a** was used. [d] 2.5 equiv of **2a** was used.

suppress the O−H insertion, and consequently afforded **4a** in 38% yield (entries 8 and 9). Considering the high conversion observed with toluene as the solvent, gratifyingly, use of the mixed solvent system of MeCN/PhMe (1:10) markedly enhanced the reaction efficiency (entry 13). Finally, raising the reaction temperature to 80 °C improved the yield to 92% (entry 14).

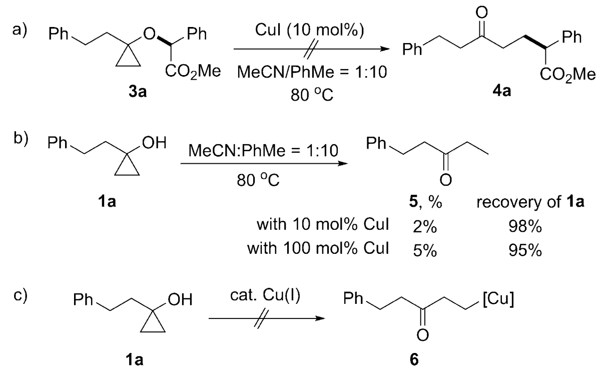
Subsequently, we proceeded to study the scope of this ring-opening/coupling reaction (Scheme 2). A series of cyclopropanols (**1a–n**), readily prepared by a Kulinkovich reaction, was first examined. The alkyl-substituted cyclopropanols (**1a–d**) reacted smoothly with the diazo ester **2a**, thus affording the corresponding products **4a–d** in good to excellent yields. Notably, a range of functional groups, such as TBS and phenyl ethers, esters, and sulfonates, are compatible with the reaction conditions (**4e–h**). Moreover, alkenyl-substituted cyclopropanols (**1i** and **1j**) are also competent substrates. Next, a series of aryl-substituted cyclopropanols **1ka–kc** were subjected to the reaction, and the desired products **4ka–kc** were obtained in good to excellent yields. It is noteworthy that when the 1,2-disubstituted cyclopropanol **1l** was used as the substrate, the reaction resulted in two constitutional isomers, **4la** and **4lb**, thus indicating that both proximal C−C bonds can be cleaved. However, both products show poor diastereoselectivity.

The scope with respect to the diazo coupling partners was then examined (Scheme 2). A series of aryl-substituted diazoacetates (**2b–e**) was investigated. Various substituents on the aromatic ring were tolerated, and the reaction was found to be hardly affected by the electronic properties of the aryl substituents. The reaction with naphthyldiazoacetate (**2f**) also gave product **4o** in 92% yield. Moreover, using the diazo compounds with different ester moieties led to similar good yields of products (**4p–t**). Finally, the reactions with the alkyl-substituted diazoacetates **2l–o** proceeded smoothly to afford the corresponding products **4u–x** in good yields.



Scheme 2. Reaction scope. Reaction conditions are as follows if not otherwise noted: **1a–n** (0.20 mmol), **2a–q** (0.30 mmol) and CuI (10 mol%) were stirred in 0.5 mL PhMe/MeCN (10:1) at 80 °C for 2 h. All yields are those of isolated products. [a] The reaction was carried out with **1a** (0.20 mmol) and **2l–o** (0.40 mmol). TBS = *tert*-butyldimethylsilyl, Ts = 4-toluenesulfonyl.

To gain insight into the reaction mechanism, several control experiments were carried out (Scheme 3). First, **3a** was treated under standard reaction conditions (Scheme 3a).



Scheme 3. Experiments for mechanistic understanding.

After stirring for 2 hours, no corresponding product **4a** was observed, thus indicating that the formation of **3a** and **4a** follows different reaction paths. Subsequently, **1a** was treated with 10 mol% CuI (Scheme 3b). After stirring for 2 hours, 98% of **1a** was recovered and only 2% of the ketone **5** (ring-opening product of **1a**) was observed. Increasing the amount of CuI to 100 mol% resulted in 5% of **5**. These results indicate that CuI alone is not effective to induce the cyclopropanol ring-opening to generate the alkyl copper intermediate **6** (Scheme 3c).[9] Thus, it is reasonable to hypothesize that the copper(I) catalyst first reacts with the diazo substrate to generate an active intermediate, which further reacts with the cyclopropanol substrate.

To gain further understanding of the reaction mechanism and in particular the chemoselectivity of O−H insertion versus ring-opening, we performed DFT calculations. Although the chemoselectivity of the ring-opening is obviously improved by MeCN as a cosolvent, as a result of the unclear formation of the $[Cu(MeCN)_n]^+$ complex we have used bipy as the ligand for computational study. Notably, the reaction with either bipy or (4*R*,4′*R*)-4,4′-dibenzyl-4,4′,5,5′-tetrahydro-2,2′-bioxazole as a ligand in toluene gave similar chemoselective ring-opening.[13] The calculations were performed on the reaction of the cyclopropanol **1k** and Cu^I carbene **A** using bipy as the ligand. All the DFT calculations were performed using Gaussian 09 (Revision A.02).[14] Geometry optimizations were carried out with B3LYP level of theory.[15] Lanl2dz basis set[16] was used for copper and 6-31G(d,p) basis set[17] for other atoms (Keyword 5D was used for calculations). The vibrational frequencies were computed at the same level to check whether the optimized structure is an energy minimum or a transition state, and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 353 K. All the transition states have been verified by IRC (intrinsic reaction coordinate) calculations. Quasi-harmonic corrections were applied for the evaluation of the entropic corrections to the Gibbs free energies by setting the frequencies less than 100 cm^{-1} to 100 cm^{-1}.[18] And the single-point energies were calculated at the M06/6-311+G(d,p) [Lanl2dz, for Cu] level of theory using the SMD model[19] with toluene as the solvent based on the B3LYP/6-31G(d,p)[Lan2lzd, for Cu] optimized geometries.[20] The calculated Gibbs free energies are determined by adding the thermal correction to Gibbs free energies, based on the B3LYP level of theory, and single-point energy with solvation energy correction based on the M06 level of theory. Gibbs free energies for all species were corrected by a factor of RTln(29.0) from 1 atmosphere of gas to 1 M solution for standard-state corrections, corresponding to 2.4 kcal mol^{-1}. Figure 1 illustrates the free energy profiles of two reaction pathways: O−H insertion for C−O bond formation and ring-opening for C−C bond formation. Figure 2 gives key intermediates and transition-state structures, which were prepared with CYLview.[21]

The mechanisms of O−H insertion of diazo compounds with either rhodium or copper as catalysts have been previously studied in detail with DFT calculations.[22] For comparison, DFT studies with O−H insertion have also been investigated for the current reaction system. In Figure 1, calculations show that in the O−H insertion process, nucle-

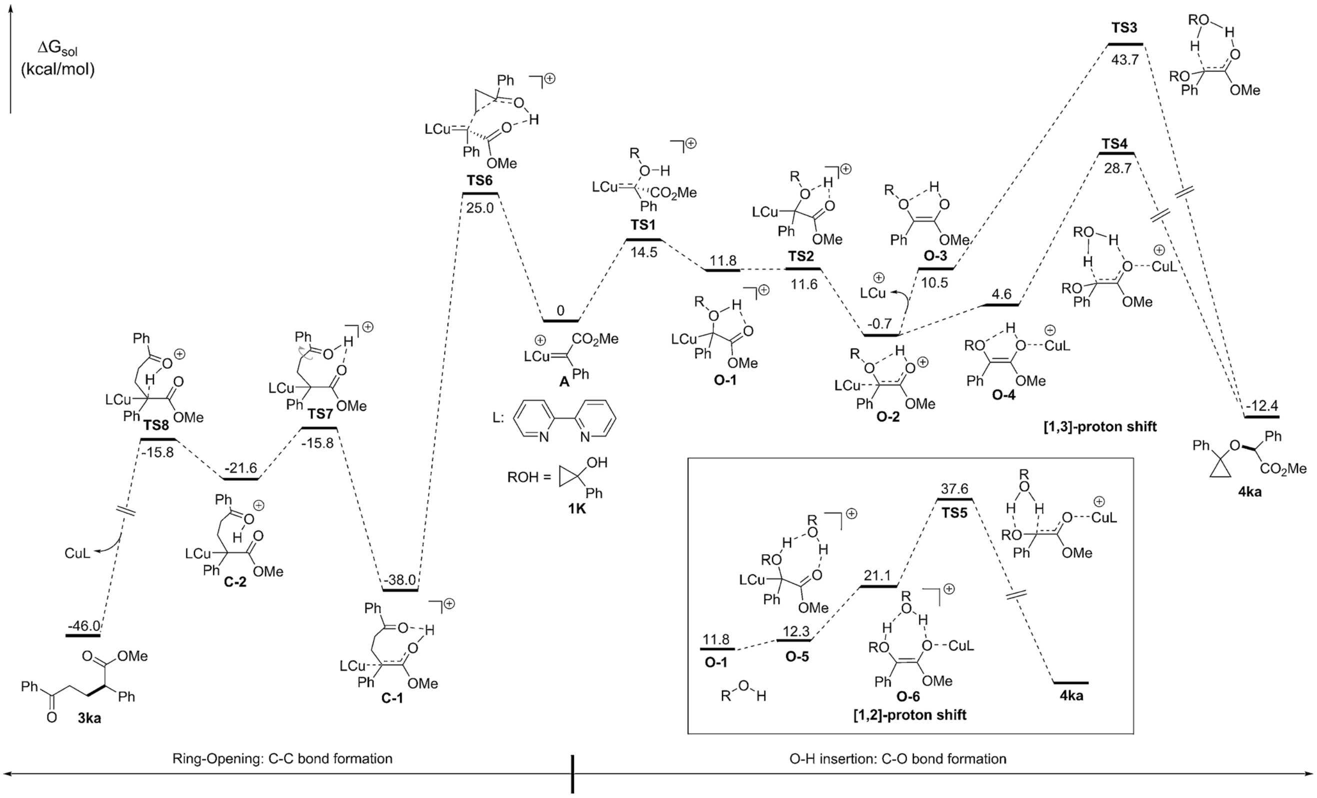
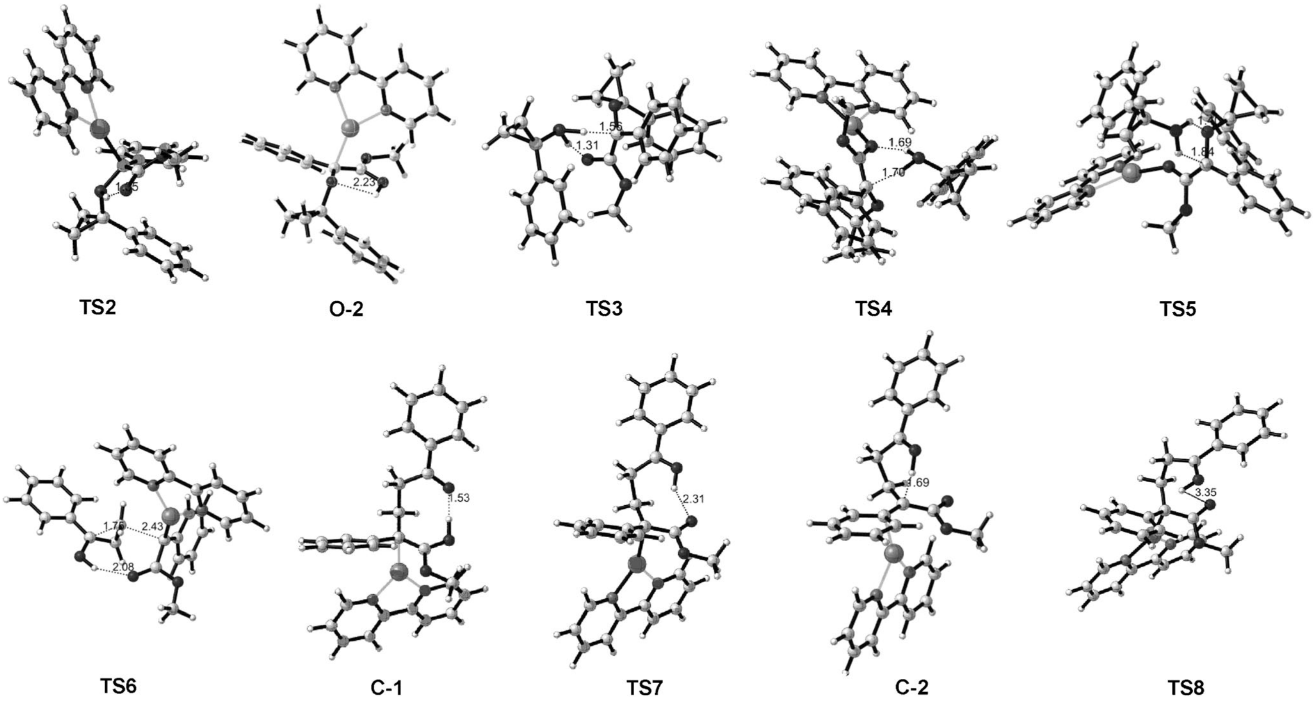


Figure 1. DFT-computed free-energy surface for the copper-catalyzed carbene O−H insertion and ring-opening/$C(sp^3)$−$C(sp^3)$ bond formation.



TS2 O-2 TS3 TS4 TS5

TS6 C-1 TS7 C-2 TS8

Figure 2. DFT-computed key intermediates and transition states.

ophilic attack of **1k** on **A** is very facile through transition-state **TS1** with an activation free energy of 14.5 kcal mol^{-1}. In **TS1**, the distance between the hydrogen atom of O−H and the oxygen atom of C=O is 1.66 Å, thus indicating a hydrogen-bonding interaction. The formation of the oxonium ylide **O-1** is endergonic by 11.8 kcal mol^{-1}. For **O-1**, the formed C−O bond has a bond length of 1.59 Å, while the C−O bond (1.41 Å) in **1k** and C=Cu (1.89 Å) bond in **A** are elongated to 1.49 Å and 2.01 Å, respectively. The previous studies by Yu and co-workers have suggested that the formation of O−H insertion product, by a H-shift process of the metal-dissociated oxonium ylide, has a higher energy barrier because of the difficulty of an intramolecular [1,2] proton shift.[22a,23] Therefore, the H-shift processes with metal-associated oxonium ylide are also anticipated in the current reaction. Here we have found that **O-1** can convert into the metal-associated enol intermediate **O-2** quickly via **TS2** with an activation free energy of nearly 0 kcal mol^{-1}. In **TS2**, the formed C−O bond is shortened to 1.54 Å and the elongation of C=Cu bond is only 0.02 Å with the respect of **O-1**, thus indicating that a low activation energy barrier is attributed to the minor geometrical variation. Then formation of the copper dissociated **O-3** from **O-2** is endergonic by 11.4 kcal mol^{-1}. Subsequent [1,3] proton shift via **TS3**, assisted by **1k**, has an energy barrier of 33.2 kcal mol^{-1}. Thus, the overall energy barrier of this pathway is as high as 44.4 kcal mol^{-1}, indicating that the metal-free [1,3] proton shift pathway is unlikely, and is consistent with the study by Yu and co-workers.[22] Alternatively, **O-2** can be transferred into **O-4** with the oxygen atom coordinated to the copper, and is endergonic by only 5.3 kcal mol^{-1}. The following cyclopropanol-assisted [1,3] proton shift via **TS4** leads to the O−H insertion product **4ka**, crossing an overall energy barrier of 29.4 kcal mol^{-1}.

In the previous computational studies by Yu[22a] and Xie[22b] on copper(I)-catalyzed carbene O−H insertion, a water-catalyzed [1,2] proton shift pathway was proposed. We have also carried out DFT calculations on the similar cyclopropanol-assisted [1,2] proton shift in our reaction system (Figure 1, inset). The oxonium ylide **O-1** interacts with **1k** through hydrogen bonding, thus generating **O-5**. The process is slightly endergonic by 0.5 kcal mol^{-1}. The intermediate **O-5** is further converted into the enol-copper intermediate **O-6**, which undergoes a [1,2] proton shift via a five-membered ring transition-state (**TS5**) to give the O−H insertion product **4ka**. In this pathway, the overall energy barrier is 37.6 kcal mol^{-1}, which is higher than that of [1,3] proton pathway described above (29.4 kcal mol^{-1}).

In contrast to O−H insertion, **1k** can also react with **A** via the transition-state **TS6**, in which **1k**, as the carbon nucleophile reacts with copper(I) carbene by ring-opening. The energy barrier for this pathway is 25.0 kcal mol^{-1}. In **TS6**, the formed C−C bond has a bond length of 2.43 Å, which is much longer than a single C−C bond (1.54 Å), thus suggesting an early transition state. The distance between O−H hydrogen atom and the carbonyl oxygen atom is 2.08 Å, thus indicating the formation of a hydrogen bond. The elongation of the C−C bond of the three-membered ring is 0.25 Å, while the elongation of C=Cu is only 0.04 Å. The high activation energy is attributed to the broken C−C bond of the cyclopropane moiety. However, this step, leading to the formation of the enol intermediate **C-1**, is dramatically exothermic by 38.0 kcal mol^{-1} because of the release of ring-strain. This data suggests that this step is irreversible. **C-1** can transfer into the intermediate **C-2** via the transition-state **TS7** with an activation energy of 22.2 kcal mol^{-1}. **C-2** is quickly converted into the final product by a [1,5] proton shift via **TS8**, thus crossing an activation free energy of only 5.8 kcal mol^{-1}.

Therefore, the DFT calculations show that the ring-opening pathway via the rate-determining and irreversible **TS6** has an activation barrier of 25.0 kcal mol^{-1}, while O–H insertion via the rate-determining **TS4** needs 28.7 kcal mol^{-1}, thus suggesting the formation of C–C cleavage product is kinetically favored by 3.7 kcal mol^{-1}. Therefore, the C–C bond cleavage product will be predominant as compared to the O–H insertion product, which is consistent with the experimental observations.

In summary, we have developed a copper(I)-catalyzed coupling of cyclopropanols with diazo esters to provide ring-opened/C(sp^3)–C(sp^3) coupled products, whereas the conventional carbene O–H insertion pathway can be mostly suppressed. DFT calculations provide insights into the detailed reaction mechanism and the rationale for this exceptional chemoselectivity.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbenes · C–C coupling reactions · copper · diazo compounds · small ring compounds

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Communications

C–C Coupling Reactions

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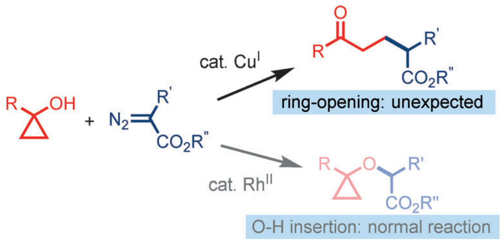
Copper(I)-Catalyzed Chemoselective Coupling of Cyclopropanols with Diazoesters: Ring-Opening C–C Bond Formations



Making the transfer: Under copper(I)-catalyzed reaction conditions, the reaction of cyclopropanols with diazo esters gives ring-opening/C(sp^3)–C(sp^3) bond-forming products rather than the conventional O–H insertion products. A rationale for this unusual chemoselectivity is provided by computational studies.