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N-Heterocyclic Carbene (NHC)-Catalyzed Intermolecular Hydroacylation of Cyclopropenes

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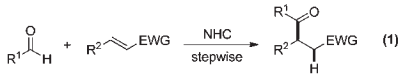
Supporting Information

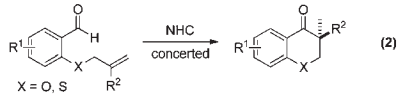
ABSTRACT: We report the first intermolecular NHC-catalyzed hydroacylation of electron-neutral olefins. Treatment of aromatic aldehydes with cyclopropenes under mild conditions affords valuable acylcyclopropanes in moderate to high yields with an excellent level of diastereocontrol. Preliminary mechanistic studies suggest that product formation occurs via a concerted *syn* hydroacylation pathway.

The use of N-heterocyclic carbenes (NHCs) as organocatalysts provides a unique activation mode of aldehydes, inverting their innate reactivity by rendering the carbonyl carbon nucleophilic.[1] This Umpolung strategy has notably been applied in the Stetter reaction, the addition of aldehydes to Michael acceptors (eq 1).[2] Extensive studies in this field culminated in elegant reports on both *intra-* and *intermolecular* variants of this transformation with excellent stereochemical control.[3] In 2009, our group reported the first intramolecular hydroacylation of electron-neutral olefins to afford substituted chromanones (eq 2).[4] More recently, we demonstrated that this transformation can be performed in a highly enantioselective fashion[5] and be further extended to alkynes.[6] Our theoretical studies suggest a concerted although highly asynchronous hydroacylation pathway, which differs substantially from the stepwise mechanism generally accepted for the Stetter reaction.[7] To increase the utility of this new mode of reactivity in NHC organocatalysis, an *intermolecular* variant would be highly desirable (eq 3).

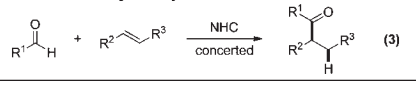
An extensively studied transformation: the Stetter reaction



***Intramolecular* NHC-catalyzed hydroacylation of electron-neutral olefins**



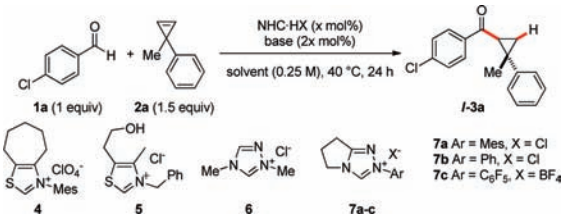
A remaining challenge in organocatalysis: *intermolecular* hydroacylation of electron-neutral olefins



Cyclopropenes represent versatile synthetic building blocks and exhibit special reactivity because of their inherent ring strain.[8] These properties have already been widely exploited in metal-catalyzed processes.[9] Notably, the group of Vy Dong recently described a Rh-catalyzed method for the highly enantioselective hydroacylation of cyclopropenes with salicylaldehydes.[10] In contrast, cyclopropenes have rarely been reported as substrates in organocatalysis.[11a] Furthermore, the use of electron-neutral olefins in organocatalyzed processes remains a virtually unmet challenge.[11] Herein we report the NHC-catalyzed hydroacylation of cyclopropenes, an unprecedented intermolecular organocatalyzed addition to electron-neutral olefins. It is characterized by a broad substrate scope with excellent diastereocontrol and affords densely functionalized acylcyclopropanes.[12]

4-Chlorobenzaldehyde **1a** and 3-methyl-3-phenylcyclopropene **2a**[13] were chosen as model substrates to optimize the reaction conditions (Table 1). We began our study with thiazolium

Table 1. Optimization of Reaction Conditions[a]



entry	NHC•HX (x mol%)	base	solvent	yield (%)[b]	dr[c] (l:u)
1	**4** (20)	K_2CO_3	THF	42	>20:1
2	**5** (20)	K_2CO_3	THF	<5	–
3	**6** (20)	K_2CO_3	THF	5	–
4	**7a** (20)	K_2CO_3	THF	93	>15:1
5	**7b** (20)	K_2CO_3	THF	<5	–
6	**7c** (20)	K_2CO_3	THF	<5	–
7	**7a** (20)	DBU	THF	82	>20:1
8	**7a** (20)	KHMDS	THF	48	3.5:1
9	**7a** (10)	K_2CO_3	THF	94	>20:1
10	**7a** (5)	K_2CO_3	THF	88	>20:1
11	**7a** (5)	K_2CO_3	toluene	28	14:1
12	**7a** (5)	K_2CO_3	*t*-amylOH	41	10:1
13	**7a** (5)	K_2CO_3[d]	THF	>99 (91[e])	>20:1

[a] Conditions: **1a** (0.1 or 0.2 mmol, 1 equiv), **2a** (1.5 equiv), NHC•HX (x mol%), base ($2x$ mol%), solvent (0.25 M), 40 °C, 24 h. [b] Yield determined by ^{1}H NMR of the crude product using CH_2Br_2 as the internal standard. [c] Diastereomeric ratios determined by ^{1}H NMR. [d] 1.0 equiv of base was used. [e] Yield after purification.

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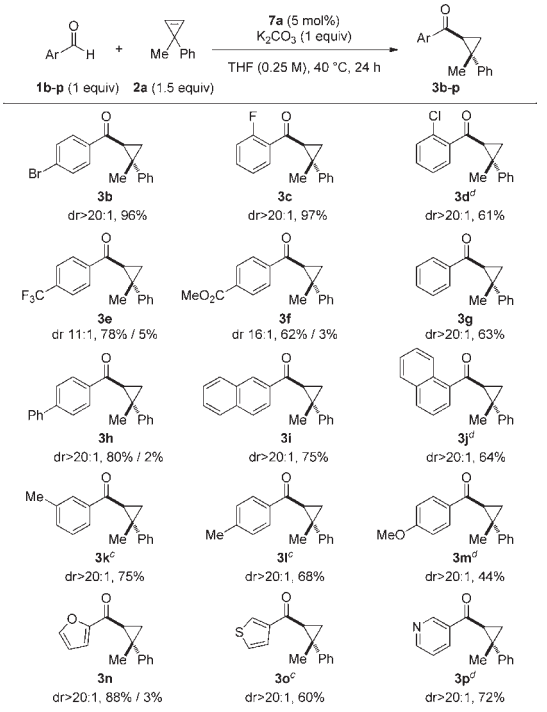
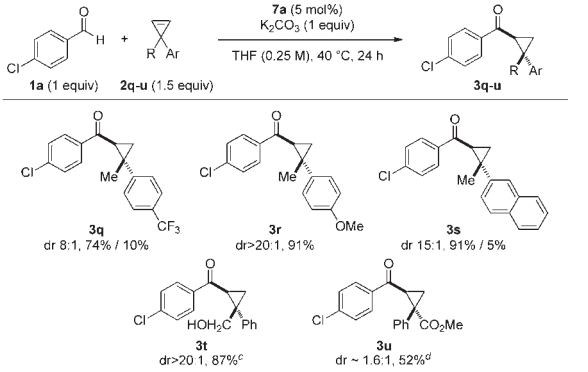
Table 2. Variations of Aromatic Aldehyde[a,b]



[a] Conditions: aldehyde **1b**−**p** (0.5 or 1 mmol, 1 equiv), cyclopropene **2a** (1.5 equiv), NHC•HX (5 mol%), K_2CO_3 (1 equiv), THF (0.25 M), 40 °C, 24 h. [b] Diastereomeric ratios as determined by ^{1}H NMR and yield of the major *l*-acylcyclopropanes **3b**−**p** after purification are shown. For some substrates, a small amount of the *u*-diastereoisomer could also be isolated (second yield). [c] 10 mol% of **7a** was used. [d] 20 mol% of **7a** was used.

Table 3. Variations of Cyclopropene[a,b]



[a] Conditions: aldehyde **1b**−**p** (1 mmol, 1 equiv), cyclopropene **2a** (1.5 equiv), NHC•HX (5 mol%), K_2CO_3 (1 equiv), THF (0.25 M), 40 °C, 24 h. [b] Diastereomeric ratios as determined by ^{1}H NMR and yield of the major *l*-acylcyclopropanes **3q**−**u** after purification are shown. For some substrates, a small amount of the *u*-diastereoisomer could also be isolated (second yield). [c] Product **3t** is in equilibrium with its closed, hemiketal form and was characterized as its corresponding *tert*-butyldimethylsilylether. The yield over two steps is shown.[15] [d] 10 mol% of **7a** was used.

salt **4**, which had consistently shown excellent reactivity in our previous hydroacylation reactions.[4a,6,14] With K_2CO_3 as the base and THF as the solvent, acylcyclopropane **3a** was obtained in an encouraging yield and very high diastereoselectivity (Table 1, entry 1). NOE studies secured the structure of the major product as the *like*-diastereomer *l*-**3a**.[15] A survey of carbene precursors showed that whereas thiazolium salt **5** and triazolium salt **6** gave no to little formation of the desired product (entry 2 and 3), the mesityl-substituted triazolium salt **7a**[16] was particularly efficient, providing **3a** in quantitative yield (entry 4). Interestingly, the phenyl- and pentafluorophenyl-substituted analogues **7b**−**c** were completely ineffective (entries 5 and 6).[17] Stronger bases such as DBU and KHMDS proved detrimental to the conversion and/or diastereoselectivity (entries 7 and 8). The catalyst loading could be lowered to 10 mol% without any influence on the reaction outcome, but a further decrease to 5 mol% slightly reduced the conversion (entries 9 and 10). At this stage, various solvents were screened, but both apolar and polar protic solvents were inferior to THF (entries 11 and 12). In the end, by increasing the amount of base, full conversion could be restored with only 5 mol% of the catalyst without compromising the diastereoselectivity (entry 13).

With this optimized condition in hand, we sought to examine the generality of this transformation (Table 2). A variety of aromatic aldehydes successfully underwent hydroacylation.[18] The amount of triazolium catalyst employed was adapted based on the reactivity of the substrates to achieve full conversion.[19] Halogen-substituted benzaldehydes reacted efficiently, and the resulting acylcyclopropanes **3b** and **3c** were obtained in high yields and diastereoselectivities. A higher catalyst loading (20 mol%) was necessary for the more sterically demanding 2-chlorobenzaldehyde to improve the yield of product **3d**. Aldehydes bearing electron-withdrawing functionalities, such as a *p*-trifluoromethyl or *p*-methoxycarbonyl group, were found to react with a slight decrease in diastereocontrol and constituted the only substrates where the product diastereomeric ratios were <20:1. Nonetheless **3e** and **3f** were isolated in reasonable yields. The parent benzaldehyde and other electronically similar aldehydes also exhibited excellent reactivity, affording products **3g**,[20] **3h**, and **3i** in moderate to good yields. The sterically demanding 1-naphthaldehyde showed lower reactivity, and 20 mol% of catalyst was required to obtain 1-naphthyl-substituted derivative **3j**. Aldehydes bearing electron-donating substituents generally represent more challenging substrates in NHC organocatalysis and similarly in the present reaction. Increasing the catalyst loading to 10 mol% however allowed the isolation of 3- and 4-methyl-substituted derivatives **3k** and **3l** in good yields. The electron-rich methoxy functionality was also tolerated, and acylcyclopropane **3m** could be obtained with superb diastereocontrol, albeit in moderate yield.[21] Additionally, heteroaromatic aldehydes participated successfully in this hydroacylation reaction. 2-Furyl-, 3-thiophenyl-, and 3-pyridyl substituted products **3n**−**p** were isolated with yields comparable to their carbocyclic analogues. Salicylaldehyde gave no detectable amount of the desired product.[22] In contrast to the known method where an *ortho*-hydroxyl functionality on the aldehyde coupling partner appeared to be necessary,[10] our organocatalytic method provides a novel range of substrates that complements existing metal-catalyzed processes.

We next examined the reaction with a range of cyclopropenes. Other 3-methyl-substituted cyclopropenes reacted similarly to the parent compound **2a**. Electron-withdrawing, electron-donating, and polyaromatic groups were all well tolerated. 4-(Trifluoromethyl)phenyl-substituted acylcyclopropane **3q** was obtained in a good yield but with reduced diastereoselectivity (8:1), whereas its 4-methoxy and 4-naphthyl analogues **3r** and **3s** were formed in a highly selective manner (Table 3). Similar

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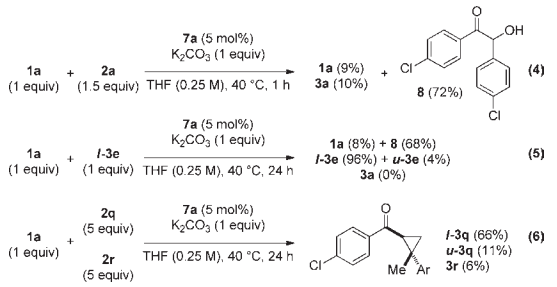
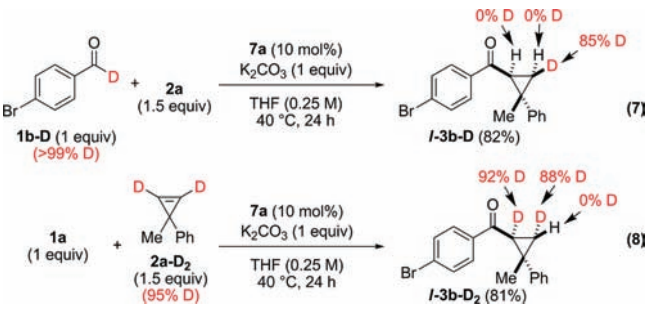
Scheme 1. Study on the General Reaction Pathway[a]



[a] Yields determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

Scheme 2. Deuterium Labeling Studies[a]



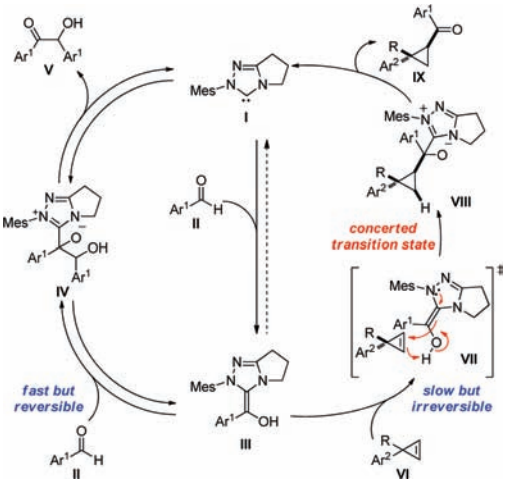
[a] Yields of *l*-acylcyclopropane **3b** after purification.

reactivity was observed when the second substituent at the quaternary carbon of the cyclopropene was varied to a hydroxymethyl group, providing **3t** in good yield. A methyl ester functionality however drastically affected both the reactivity and the diastereoselectivity: Contrary to other examples, the diastereoselectivity of the major product **3u** arises from attack of the Breslow intermediate from the face of the phenyl group.[23]

To gain further mechanistic insight, a series of experiments were designed to probe the kinetics of the reaction (Scheme 1).[15,24] After 1 h of reaction, 4-chlorobenzoin **8** was observed as the major product (72%), with a small amount of the starting aldehyde **1a** and the product **3a** (eq 4). When benzoin was subjected to the optimized reaction condition, the desired hydroacylation product **3g** could be formed in 84% yield. To test the stability of the product under the reaction condition, *l*-4-trifluoromethyl-substituted **3e** was introduced to the reaction of 4-chlorobenzaldehyde **1a** with triazolium salt **7a** (eq 5). No detectable formation of the crossover product, (4-chlorophenyl)acylcyclopropane **3a**, was observed after 24 h. **3e** was recovered quantitatively, but with slight epimerization (4%). These observations indicate that benzoin formation is reversible, whereas addition of the Breslow intermediate to the cyclopropene is irreversible. In a competition experiment between the two electronically different cyclopropenes **2q** and **2r** (eq 6), the electron-poor **2q** reacted more than ten times faster than the more electron-rich **2r**. This result further confirmed that the union of the two fragments is involved in the rate-determining step of the catalytic cycle.

To investigate the nature of the hydroacylation step, a number of deuterium labeling experiments were carried out (Scheme 2). When deuterated 4-bromobenzaldehyde **1b-D**[25] was used, the deuterium was incorporated exclusively *cis* to the acyl group to give product **3b-D** (eq 7).[15,26] Addition of the Breslow intermediate derived from **1b** to 1,2-dideuterocyclopropene **2a-D$_2$**[27] provided the *cis*-dideuterated product **3b-D$_2$** as the only product (eq 8). Because computational studies on stepwise anionic addition to cyclopropenes[8b] have indicated formation of the negative charge *anti* to the incoming nucleophile, the observed *syn*-deuterium incorporation is consistent with a concerted addition mechanism,[28] as previously suggested by DFT calculations for the NHC-catalyzed intramolecular hydroacylation of electron-neutral olefins.[5]

Scheme 3. Proposed Catalytic Cycle



Based on the results of our preliminary mechanistic investigation, we propose a plausible catalytic cycle as outlined in Scheme 3. First, the nucleophilic Breslow intermediate **III** is formed through the addition of NHC **I** to aldehyde **II** followed by proton transfer. **III** then quickly combines with a second molecule of aldehyde **II**. The tetrahedral intermediate **IV** collapses to give benzoin **V** as the kinetic product and regenerates the carbene catalyst. This sequence represents a *reversible* process and the Breslow intermediate can be formed anew to allow a slow, but *irreversible*, attack on cyclopropene **VI** to give intermediate **VIII**, which affords the desired acylcyclopropane **IX**. The diastereospecific nature of this last step, supported by our deuteration studies, points toward a *concerted* transition state such as **VII**.[29] The observed diastereoselectivity is derived from steric minimization, with the more bulky aromatic group Ar^2 being placed preferentially away from the aryl substituents of the NHC. Additionally, we hypothesize that potential hyperconjugative interactions between the forming C−C bond and the antiperiplanar $\sigma^*_{C-Ar^2}$ bond could provide additional stabilization in the diastereomeric transition state leading to the observed *l*-acylcyclopropane.[30,31]

We have developed an organocatalytic intermolecular addition of aldehydes to cyclopropenes under mild conditions. This methodology allows for a highly convergent and efficient formation of functionalized acylcyclopropanes with excellent diastereocontrol. Our mechanistic investigation provides experimental evidence for a diastereospecific hydroacylation step, which is in accordance with a concerted mechanism.[5] This novel reactivity mode of NHC organocatalysis carries mechanistic impact on related transformations and should find further interesting applications.

■ ASSOCIATED CONTENT

Supporting Information. Experimental section and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Linear and branched aliphatic aldehydes did not undergo the hydroacylation reaction, affording only traces of the desired product along with the nearly quantitative formation of acyloin even under more forcing conditions (20 mol% of catalyst at 80 °C).

(19) Attempts to improve the yield or diastereoselectivity by varying the temperature of the reaction proved ineffective.

(20) Only product **3g** is previously reported in the literature: (a) Nishimura, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2001**, *66*, 1455. (b) Auricchio, S.; Grassi, S.; Malpezzi, L.; Sarzi Sartori, A.; Truscello, A. M. *Eur. J. Org. Chem.* **2001**, 1183.

(21) Substrates with a combination of electron-richness and steric hindrance gave little amount of the desired product. For example, 2-methoxybenzaldehyde showed less than 20% conversion with 20 mol% of the triazolium catalyst (data not shown).

(22) This result is consistent with our observation that electron-rich aldehydes exhibit lower reactivity.

(23) This is consistent with our hypothesis on the origin of diastereoselectivity, vide infra. See refs 30 and 31.

(24) The control experiment without triazolium salt **7a** or K_2CO_3 showed no detectable formation of the hydroacylated product **3a**, see ref 15.

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(26) It amounted to only 85%, most likely due to scrambling with the proton of triazolium salt **7a** in the equilibrating process between benzoin and retro-benzoin.

(27) Prepared by adapting a known procedure: Alnasleh, B. K.; Sherrill, W. M.; Rubin, M. *Org. Lett.* **2008**, *10*, 3231. See Supporting Information for more details and complete characterization.

(28) Because cyclopropyl anions are observed to be configurationally stable (see Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3283), *anti*-deuterium incorporation would have been observed based on a stepwise mechanism.[8b] Alternatively, it is also possible that, in a stepwise addition process, formation of the negative charge occurs *syn* to the Breslow intermediate for electrostatic stabilization. The corresponding stepwise mechanism therefore cannot at this point be excluded.

(29) For related noncatalytic additions to electron-neutral alkenes proceeding through a five-membered concerted transition state, see: (a) Oppolzer, W.; Spivey, A. C.; Bochet, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 3139. (b) Beauchemin, A. M.; Moran, J.; Lebrun, M.-E.; Séguin, C.; Dimitrijevic, E.; Zhang, L.; Gorelsky, S. I. *Angew. Chem., Int. Ed.* **2008**, *47*, 1410.

(30) For discussions on the hyperconjugative stabilization in addition reactions, see: Houk, K.; Paddon-Row, M.; Rondan, N.; Wu, Y.; Brown, F.; Spellmeyer, D.; Metz, J.; Li, Y.; Loncharich, R. *Science* **1986**, *231*, 1108.

(31) This is consistent with our observation that the opposite diastereoselectivity was observed in the reaction of substrate **2u**, where the $\sigma^*_{C-CO_2Me}$ bond is a better acceptor than the σ^*_{C-Ar}[2].