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Regiodivergent Lewis base-promoted *O*- to *C*-carboxyl transfer of furanyl carbonates†

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Triazolinylidenes promote γ-selective C-carboxylation (up to 99 : 1 regioselectivity) in the *O*- to *C*-carboxyl transfer of furanyl carbonates in contrast to DMAP that promotes preferential α-C-carboxylation with moderate regiocontrol (typically 60 : 40 regioselectivity). The generality of this process is described and a simple mechanistic and kinetic model postulated to account for the observed regioselectivity

Introduction

The butenolide architecture is recognized as a privileged structure in synthetic chemistry, and is present in a variety of biologically active natural products.[1] The preparation of functionalized butenolides is commonly achieved by generation of the corresponding furanyl dienolate and reaction with an appropriate electrophile, with alkylations, vinylogous Mukaiyama–aldol, Mukaiyama–Michael and Mukaiyama–Mannich reactions all extensively explored, generally giving high levels of selectivity for γ-functionalization.[2] Limited catalytic methodologies have been developed with the formation of quaternary centers, although a number of organocatalytic[3] and metal-catalyzed processes show promise in this area.[4] As an alternative strategy to generate quaternary-functionalized butenolides, Vedejs *et al.* have investigated the Lewis base[5]-promoted regio- and enantioselective *O*- to *C*-carboxyl transfer of 5-aryl-3-methylfuranyl carbonates **1** using TADMAP **2**.[6] In this process, the electronic characteristics of the C(5)-aryl substituent markedly affects the observed regioselectivity of this carboxyl transfer process. For example, while a C(5)-phenyl furanyl carbonate gave a 60 : 40 mixture of α : γ products, an electron-donating C(5)-4-MeOC₆H₄ substituent favored α-functionalization (α : γ up to 92 : 8) while an electron-with-

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drawing C(5)-4-NCC₆H₄ substituent favored γ-functionalization (α : γ up to 20 : 80) (Fig. 1).

Building upon our interest in Lewis base catalysis[7,8] and *O*-to *C*-carboxyl transfer rearrangements,[9] we have recently developed a catalyst selective regiodivergent *O*- to *C*- or *N*-carboxyl transfer reaction of pyrazolyl carbonates (Fig. 2, eqn (1)).[10] In this process, NHCs promote selective *O*- to *C*-carboxyl transfer, while DMAP promotes selective *O*- to *N*-transfer, with quantum mechanics calculations used to probe the observed catalyst selective divergence. In this manuscript we probe the generality of this principle by application to the *O*- to *C*-carboxyl transfer of furanyl carbonates. We sought to apply this catalyst selective[11] regiodivergence to promote γ-C-carboxylation in this process that would be independent of the electronic nature of furanyl substitution, allowing a direct comparison with the electronic bias observed by Vedejs.[12] In this manuscript (Fig. 2, eqn (2)), triazolinylidene NHCs promote highly γ-selective C-carboxylation of furanyl carbonates in this rearrangement process (regioselectivity up to 1 : 99 α : γ), while DMAP gives preferential, but modest, α-selectivity (regioselectivity typically 60 : 40 α : γ).

Results and discussion

Model studies: regioselective *O*- to *C*-carboxyl transfer of furanyl carbonate 5

Initial studies probed the effectiveness of archetypal amine-centered Lewis bases 4-dimethylaminopyridine **3** (DMAP) and isothiourea 3,4-dihydro-2*H*-pyrimido[2,1-*b*]benzothiazole **4** (DHPB) to promote the γ-regioselective rearrangement of **5**. Under standardized conditions (34 mM, 10 mol%) of the Lewis base, and with a one hour reaction time, both catalysts promoted *O*- to *C*-carboxyl transfer with modest regiocontrol, giving an approximate 60 : 40 ratio of α- : γ-products **6** : **7** (Table 1, entries 1 and 3).[13] The ability of triazolinylidene NHCs to catalyze the rearrangement of **5** was next investigated. Using KHMDS as the base to generate NHC **8** from the corresponding precatalyst gave efficient catalysis, generating a 16 : 84

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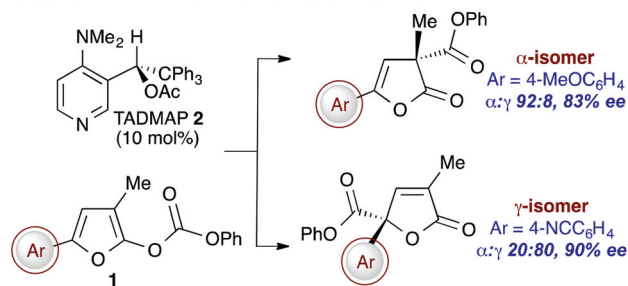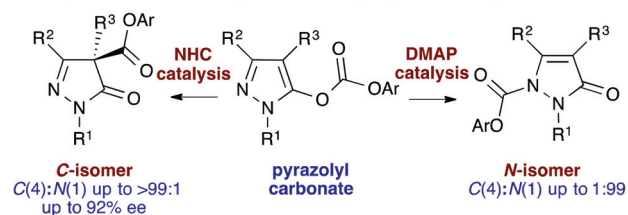*Vedejs: electronic determinant of regioselectivity*

Fig. 1 Vedejs' regioselective carboxyl transfer.

1. Our previous work: catalyst determining regioselectivity
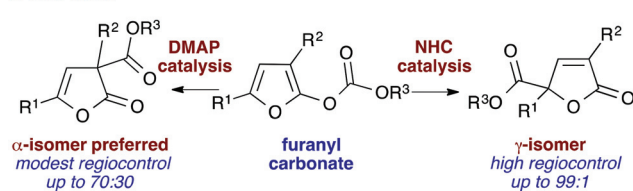
2. This work:

Fig. 2 Regiodivergent Lewis base promoted carboxyl transfer.

ratio of α-:γ-regioisomers (individual isomers were isolated in 6% and 72% yield respectively) (entry 4). Alternative N-C_6F_5 and N-4-$MeOC_6H_4$ substituted triazolinylidenes **9** and **10** give identical preferential γ-regioselectivity (entries 5–6).[14] Further investigation using NHC catalyst **8** showed that at higher NHC concentrations (~85 mM, 22.5 mol%) an identical 16 : 84 ratio of α-:γ-carboxyl products **6**:**7** was obtained. However, upon sequentially lowering the NHC concentration (to 3.4 mM, 0.9 mol% entries 7–11) the reaction still progressed rapidly to completion (<5 min), giving a 2 : 98 ratio of α-:γ-products after five minutes (entry 10), which decayed to a 4 : 96 ratio of α-:γ-products after one hour (entry 11). Further lowering of the NHC concentration (1.7 mM, 0.45 mol%) and sampling the reaction before full consumption of the carbonate starting material (1 min) showed that at 90% conversion, exclusively the γ-carboxyl product **7** was formed (entry 12). After one hour, and at full conversion, a 2 : 98 ratio of α-:γ-products was observed (entry 13). Using DMAP gave a consistent 60 : 40 ratio of α-:γ-products irrespective of concentration (34 mM, 10 mol% or 3.4 mM, 1 mol%). Unfortunately, treatment of **5** with a number of archetypal chiral NHCs in an attempt to promote the regio- and enantioselective version of this transformation returned exclusively starting material in each case.

Table 1 Regioselective *O*- to *C*-carboxyl transfer of model furanyl phenyl carbonate **5**[a]
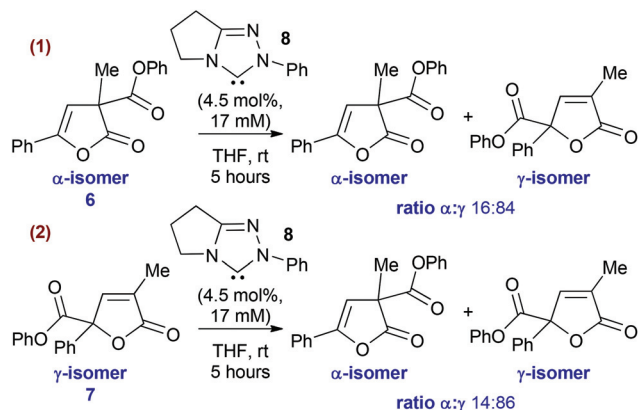

Entry	Lewis base (mol%)	[Lewis base]/ mM	Ratio **6**(α): **7**(γ)[b]	Yield[c] (%)
1[d]	DMAP **3** (10)	34	60 : 40	60 (α)
2[d]	DMAP **3** (1)	3.4	60 : 40	—
3[d]	DHPB **4** (10)	34	56 : 44	—
4[d]	NHC **8** (9)	34	16 : 84	72 (γ)
5[d]	NHC **9** (9)	34	16 : 84	—
6[d]	NHC **10** (9)	34	16 : 84	—
7[d]	NHC **8** (22.5)	85	16 : 84	—
8[d]	NHC **8** (4.5)	17	16 : 84	—
9[d]	NHC **8** (1.8)	6.8	10 : 90	—
10[e]	NHC **8** (0.9)	3.4	2 : 98	85 (γ)
11[d]	NHC **8** (0.9)	3.4	4 : 96	—
12[f]	NHC **8** (0.45)	1.7	0 : 100	—
13[d]	NHC **8** (0.45)	1.7	2 : 98	—

[a] In all cases the NHCs were prepared by prior deprotonation of the corresponding triazolium precatalyst salt with a sub-stoichiometric quantity (0.9 equiv.) of KHMDS. [b] As shown by ^{1}H NMR spectroscopic analysis of the crude reaction product. [c] Isolated yield; isomer shown in parentheses. [d] Reaction time 1 hour. [e] Reaction time 5 minutes. [f] Reaction time 1 minute.

These product distributions indicate that both DMAP **3** and NHC **8** are effective catalysts for this transformation, yet offer complementary product regioselectivities, with DMAP **3** favoring the α-isomer (with modest regiocontrol) and NHCs **8**–**10** the γ-isomer with excellent regiocontrol. To further investigate these mechanistic pathways, the individual regioisomeric products **6** and **7** were resubjected to the reaction conditions. Retreatment of both **6** and **7** with DMAP (17 mM, 5 mol%) for extended reaction times returned only the individual starting materials. However, treatment of the α-carboxyl product **6** with NHC **8** (17 mM, 4.5 mol%, five hour reaction time) returned a 16 : 84 ratio of α:γ products, consistent with significant regio-isomeric exchange to favor the γ-carboxyl product **7** (Scheme 1, eqn (1)). Similarly, treatment of the γ-carboxyl regioisomer **7** with NHC **8** (17 mM, 4.5 mol%, five hour reaction time) delivered a 14 : 86 ratio of α:γ products (eqn (2)); both ratios within experimental error of the 14 : 86 ratio observed in Table 1 at higher catalyst loadings and concentration.

The variation in ratio of α-:γ-products with NHC concentration, catalyst loading, and reaction time, suggest the inter-

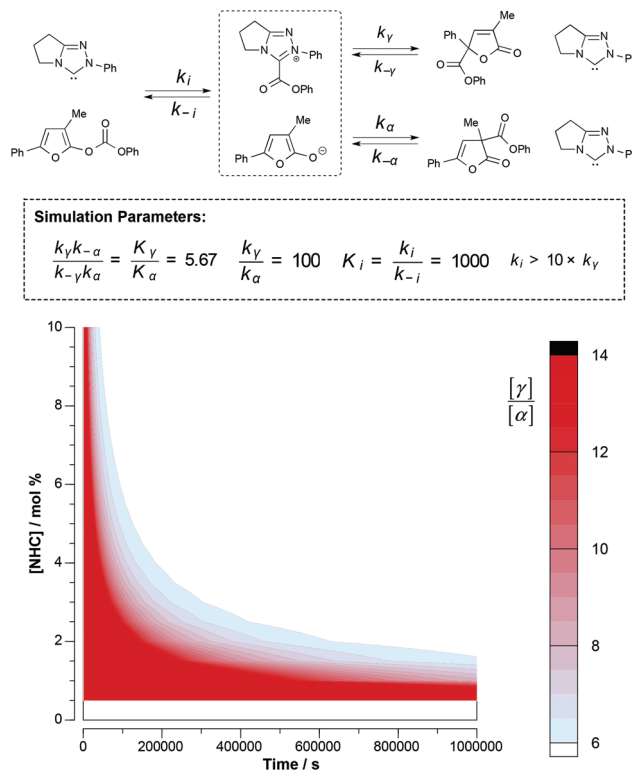**2896** | *Org. Biomol. Chem.*, 2015, **13**, 2895–2900

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Scheme 1 Retreatment experiments of individual isomers under NHC-catalysis.

Fig. 3 Postulated kinetic framework and simulation of NHC-promoted carboxyl transfer.

conversion of the α- and γ-regioisomeric products during the NHC-catalyzed reaction. These findings suggest that C-carboxylation with DMAP is *irreversible* in this system, with moderate, but preferential α-regiocontrol. Under NHC-catalysis *reversible* C-carboxylation is observed, with initial preferential formation of the γ-isomer, with subsequent equilibration leading to a mixture of α-:γ-products.[15] These observations contrast the irreversible C-carboxylation process observed in the rearrangement of oxazolyl carbonates with NHC **8**.[9a] While the origin of the regioselectivity preference observed under either DMAP or NHC-mediated catalysis is currently unknown in this system, mechanistic studies indicate extensive carbonate crossover, consistent with rapid and reversible O-transcarboxylation as an initial reaction step as previously observed for oxazolyl carbonates.[16]

A simple kinetic framework for this NHC-mediated process can be constructed and simulated (Fig. 3) by recognizing that the behavior of this system can be explained by invoking three coupled equilibria. The first process involves the rapid and reversible C-carboxylation of the NHC by the furanyl carbonate. This process is characterized by K_i, which, in our kinetic model, is arbitrarily set at a large value of 1000. Additionally, the value for the forward rate constant for this process, k_i, is the largest in the system. Formation of the α- and γ-products proceeds though two further equilibria, characterized by two further equilibrium constants $K_γ$ and $K_α$. The ratio of these two equilibrium constants ($K_γ/K_α = 5.67$) reflects the final ratio of the α- and γ-products (~85 : 15) reached at equilibrium. In this mechanism, free NHC is required both for reaction initiation from the furanyl carbonate and to allow equilibration of the C-carboxyl products. Since K_i is large with respect to both $K_γ$ and $K_α$, the concentration of free NHC will be low up to conversions in excess of 90% (based upon 10 mol% added NHC), leading to preferential kinetic formation of the γ-furanyl product. However, with increasing time and NHC concentration the α- and γ- isomers can interconvert to generate the observed thermodynamic product ratio. Interestingly, for this model to mirror the observed selectivity for the γ-product at low conversions and/or low catalyst loadings, it is necessary to
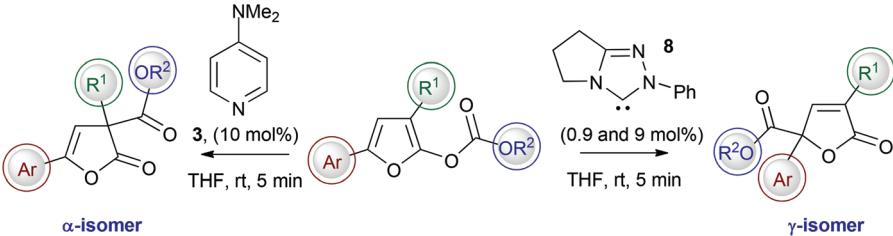
set $k_γ$ to be $100 \times k_α$ and for initiation (k_i) to be at least $10 \times k_γ$. Using this parameter set, this model correctly predicts the behavior of the experimental system – at short reaction times and low NHC loading; the system is highly γ-selective (red areas in Fig. 3). As the reaction time increases, the reactivation of the product (by addition of the NHC to product **7**) drives the system towards the thermodynamic distribution of α- and γ-isomers (white area in Fig. 3). The reasons for the differential rates of transfer to the α- and γ- positions are unclear at this stage and in future work we intend to probe these issues computationally.

Reaction generality

The generality of this regiodivergent Lewis base-promoted process was next probed (Table 2).[17] A range of furanyl carbonates varying in substitution at both C(5)- and C(3)-positions, as well as the carbonate group, were each treated with DMAP **3** (34 mM, 10 mol%) and NHC **8** (34 mM, 9 mol% or 3.4 mM, 0.9 mol%) to assess the regioselectivity of the O- to C-carboxyl transfer process. In each case DMAP **3** favored the formation of the α-isomer with modest selectivity, while the NHC **8** favored the γ-isomer with good to excellent levels of regioselectivity independent of variation of the carbonate group, as well as C(5)- and C(3)-substitution. For example, phenyl, trichloroethyl and the sterically hindered but electronically activated β,β,β-trichloro-*tert*-butyl carbonate groups are tolerated, alongside variation at C(3) from Me to Et, Bn or allyl. In all cases, using NHC-mediated catalysis optimal γ-selectivity (up to

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Table 2 Generality of the regiodivergent *O*- to *C*-carboxyl transfer of furanyl carbonates with NHC **8** or DMAP **3**

	R[1]	Ar	R[2]	Lewis base (mM, mol%)	Ratio α : γ[a]	Yield[b] (%)
1	Me	Ph	Ph	DMAP **3** (34, 10)	60 : 40	60 (α)
2				NHC **8** (34, 9)	16 : 84	72 (γ)
3				NHC **8** (3.4, 0.9)	2 : 98	85 (γ)
4	Bn	Ph	Ph	DMAP **3** (34, 10)	64 : 36	45 (α)
5				NHC **8** (34, 9)	19 : 81	67 (γ)
6				NHC **8** (3.4, 0.9)	4 : 96	67 (γ)
7	Bn	Ph	CMe$_2$CCl$_3$	DMAP **3** (34, 10)	62 : 38	56 (α); 26 (γ)
8				NHC **8** (34, 9)	4 : 96	80 (γ)
9				NHC **8** (3.4, 0.9)	1 : 99	91 (γ)
10	Bn	Ph	CH$_2$CCl$_3$	DMAP **3** (34, 10)	54 : 46	44 (α); 37 (γ)
11				NHC **8** (34, 9)	5 : 95	71 (γ)
12				NHC **8** (3.4, 0.9)	1 : 99	86 (γ)
13	Et	Ph	Ph	DMAP **3** (34, 10)	47 : 53	32 (α)
14				NHC **8** (34, 9)	21 : 79	54 (γ)
15				NHC **8** (3.4, 0.9)	1 : 99	71 (γ)
16	4-BrBn	Ph	Ph	DMAP **3** (34, 10)	53 : 47	43 (α)
17				NHC **8** (34, 9)	10 : 90	80 (γ)
18	Allyl	Ph	Ph	DMAP **3** (34, 10)	61 : 39	54 (α); 32 (γ)
19				NHC **8** (34, 9)	31 : 69	24 (α); 50 (γ)
20				NHC **8** (3.4, 0.9)	6 : 94	81 (γ)
21	Me	4-FC$_6$H$_4$	Ph	DMAP **3** (34, 10)	71 : 29	52 (α)
22				NHC **8** (34, 9)	12 : 88	67 (γ)
23				NHC **8** (3.4, 0.9)	10 : 90	71 (γ)
24	Me	4-FC$_6$H$_4$	CH$_2$CCl$_3$	DMAP **3** (34, 10)	67 : 33	60 (α)
25				NHC **8** (34, 9)	15 : 85	76 (γ)
26				NHC **8** (3.4, 0.9)	4 : 96	87 (γ)
27	Bn	4-FC$_6$H$_4$	Ph	DMAP **3** (34, 10)	71 : 29	56 (α)
28				NHC **8** (34, 9)	20 : 80	56 (γ)
29				NHC **8** (3.4, 0.9)	7 : 93	78 (γ)
30	Et	4-FC$_6$H$_4$	Ph	DMAP **3** (34, 10)	48 : 52	46 (α)
31				NHC **8** (34, 9)	20 : 80	61 (γ)
32				NHC **8** (3.4, 0.9)	4 : 96	83 (γ)

[a] As shown by ^{1}H NMR spectroscopic analysis of the crude reaction product. [b] Isolated yield.

99 : 1) is observed at lower NHC concentrations and using short reaction times, allowing the isolation of the γ-isomer in 67–91% yield.

To further probe the structural factors necessary for γ-selectivity in this NHC-mediated transformation, the rearrangement of a C(3)-phenyl–C(5)-methyl furanyl carbonate **11** was investigated. Treatment of **11** with DMAP **3** (10 mol%) gave poor regiocontrol (α : γ 57 : 43), while NHC **8** (34 mM, 9 mol% or 3.4 mM, 0.9 mol%) showed excellent control for the
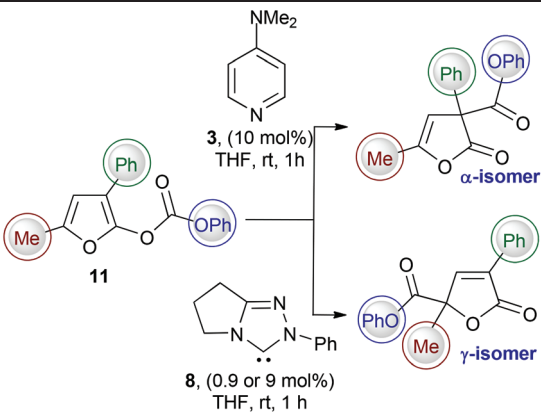
γ-isomer even after extended reaction time, consistent with γ-selective *O*- to *C*-carboxyl transfer under NHC-mediated catalysis not requiring a C(5)-aryl unit as a necessary structural feature (Table 3).[18]

Conclusions

In conclusion, under kinetic control triazolinylidenes promote γ-selective C-carboxylation (up to 99 : 1 regioselectivity) in the

Table 3 Regiodivergent *O*- to *C*-carboxyl transfer of furanyl carbonates; C(3)-phenyl substitution

Entry	Lewis base (mM, mol%)	Ratio α- : γ-[a]	Yield[b] (%)
1	DMAP **3** (34, 10)	57 : 43	48 (α)
2	NHC **8** (34, 9)	1 : 99	85 (γ)
3	NHC **8** (3.4, 0.9)	0 : 100	88 (γ)

[a] As shown by ¹H NMR spectroscopic analysis of the crude reaction product. [b] Isolated yield of major isomeric product.

O- to *C*-carboxyl transfer of furanyl carbonates, in contrast to DMAP that promotes preferential α-C-carboxylation with moderate regiocontrol. Current work from within our laboratory is focused upon demonstrating further applications of NHC-mediated organocatalytic transformations in the construction of poly-functionalized building blocks for synthesis.

Acknowledgements

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13 The formation of the parent furanone and diphenyl carbonate are minor by-products in the O- to C-carboxyl rearrangement of furanyl phenyl carbonates and typically account for <5% of the crude reaction product mixture.

14 Further investigation of this NHC-promoted protocol showed that imidazolinium or imidazolium derived NHCs (such as IMes) did not prove catalytically active in this protocol.

15 Control experiments showed that the NHC 8 is necessary for catalysis is this system, and that the furanyl dienolate (generated from the parent butenolide with KHMDS) is not catalytically active in this reaction manifold.

16 Consistent with the NHC-mediated Steglich rearrangement of oxazolyl carbonates, crossover experiments indicate an intermolecular reaction process using furanyl carbonates.

17 A range of C(3)-alkyl–C(5)-aryl furanyl carbonates were readily prepared from (phenylthio)acetic acid and an appropriate epoxide, followed by alkylation, oxidation/elimination and carbonate formation as reported previously. See ref. 9g and ESI† for full experimental details.

18 The rearrangement of **11** with either DMAP **3** or NHC **8** proceeded with a significantly retarded rate in comparison with its isomer **5**, although with similar levels of regioselectivity.

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