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Divergent Reactivity of Homologue *ortho*-Allenylbenzaldehydes Controlled by the Tether Length: Chromone versus Chromene Formation

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Dedicated to Professor Franco Fernández on the occasion of his 70th birthday and retirement

Abstract: The divergent behavior of two homologue allenals, namely, 2-(buta-2,3-dienyloxy)- and 2-(propa-1,2-dienyloxy)benzaldehydes, as cyclization substrates is described. 2-(Buta-2,3-dienyloxy)benzaldehydes suffers a formal allenic carbocyclization reaction to afford chromenes, whereas 2-(propa-1,2-dienyloxy)benzaldehydes react to yield chromones. The formation of chromenes is strictly a formal hydroarylation process divided into two parts, namely, allenic Claisen-type rearrangement and oxycyclization. An unknown N-heterocyclic carbene (NHC)-catalyzed allenic hydroacylation reaction must be invoked to account for the preparation of chromones. *ortho*-Allenylbenzaldehydes bearing either electron-donating substituents or electron-withdrawing substituents worked well to afford both the hydroarylation and hydroacylation products. This unexpected difference in reactivity can be rationalized by means of density functional theory calculations.

Introduction

Chromone derivatives constitute one of the major classes of oxygen-containing heterocycles. Their abundance in nature as well as their wide range of biological activities make chromones important synthetic targets. Among them, 3-substituted chromones deserve special attention owing to their prevalence in pharmaceutically important compounds and because of their synthetic versatility for the construction of more advanced structures.[1] As a result, efforts devoted toward the synthesis of this molecular framework remain highly desirable.

Over the course of the last decade, efforts aimed at maximizing the total efficiency of a given organic transformation and more eco-conscious disposal of chemical materials have increased. The direct formation of C–C bonds involving C–H bond cleavage is of great interest because it offers an alternative to the conventional cross-coupling strategies that require preinstallation of appropriate reactive functional groups.[2] The N-heterocyclic carbene (NHC)-catalyzed hydroacylation reaction of alkenes and alkynes is an important C–C bond-forming reaction.[3] Recently, the intramolecular hydroacylations of *ortho*-alkenylbenzaldehydes and *ortho*-alkynylbenzaldehydes were accomplished.[4] Surprisingly, the utilization of allenyl derivatives has not been explored.[5] We envisioned that *ortho*-allenylbenzaldehydes may be effective substrates for this purpose. Herein, we report a divergent reactivity of 2-(buta-2,3-dienyloxy)- and 2-(propa-1,2-dienyloxy)benzaldehydes.

Results and Discussion

Initially, we started to evaluate the intramolecular hydroacylation reaction by employing 2-(buta-2,3-dienyloxy)benzaldehyde (**1a**) as model substrate. Treatment of allenal **1a** with the NHC generated from a thiazolium salt by deprotonation with DBU did not lead to the hydroacylation adduct, ketone **2a**. Instead, 4-methyl-2*H*-chromene-8-carbaldehyde (**3a**),[6] the corresponding hydroarylation adduct, was obtained in 55% conversion and 24% isolated yield (Scheme 1). We then optimized the reaction conditions further. Chromene formation also occurred in 1,4-dioxane. When the reaction was operated in acetonitrile at reflux, we realized that the thiazolium salt was totally inefficient for the hydroarylation. However, under the same conditions the use of DBU was necessary. A control experiment showed that 3-(buta-1,3-dien-2-yl)-2-hydroxybenzaldehyde (**4a**) was formed from allenal **1a** in 1,4-dioxane at 150 °C in a sealed

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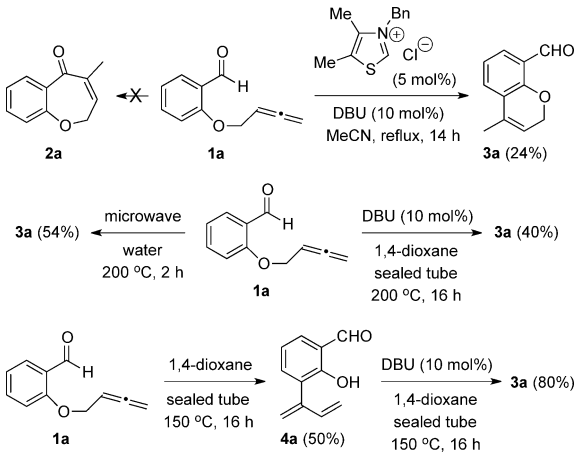
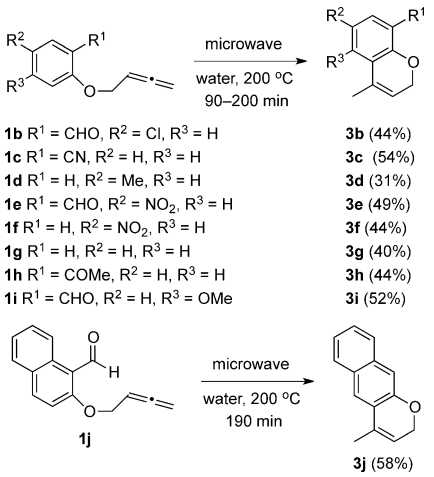


Scheme 1. Selective reactions of 2-(buta-2,3-dienyloxy)benzaldehyde (**1a**) under modified conditions. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.



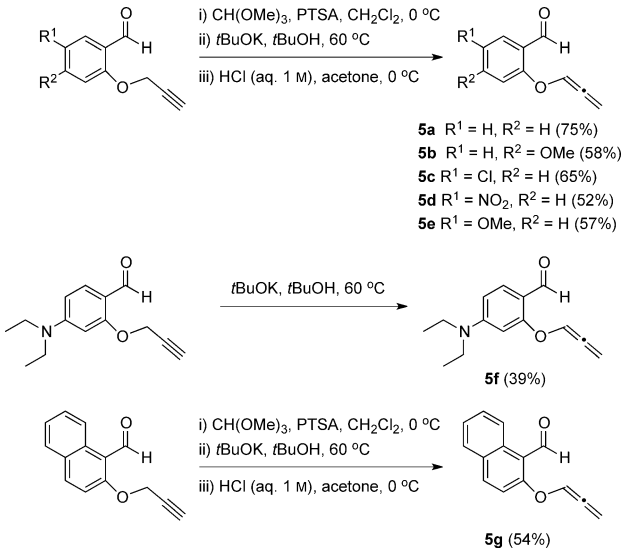
Scheme 2. Microwave-promoted preparation of chromene derivatives **3b–j**.

tube in the absence of DBU (Scheme 1). The thermal treatment of dienol **4a** in 1,4-dioxane at 150 °C in a sealed tube in the presence of DBU resulted in the formation of chromene **3a** (Scheme 1). Chromene **3a** was obtained in 40% yield from allenal **1a** when the reaction temperature was increased to 200 °C in a sealed tube. Dienol **4a** may be considered as an allenic Claisen-type rearrangement adduct. Because water may increase the efficiency of the Claisen rearrangement,[7] we decided to carry out the formal hydroarylation in water.[8] Indeed, formation of chromene **3a** can be efficiently achieved in water and microwave heating accelerates the reaction and increases the yield to 54% (Scheme 1).

Although allenal **1a** bearing a carbaldehyde group on the benzene core reacted smoothly, we needed to further probe the scope of this transformation. Allenes **1a–i** were obtained using the Crabbé reaction starting from the corresponding (prop-2-ynyloxy)benzene as described in the literature.[9] With the above optimized reaction conditions in hand, we prepared various chromene derivatives **3b–i** from allenes **1b–i** (Scheme 2). The electronic nature of the aromatic rings did not have a strong influence on the hydroarylation reaction. In fact, allenes **1** possessing both electron-rich as well as electron-deficient substituents on the aromatic ring underwent cyclization. Interestingly, tricycle **3j** was obtained from 2-(buta-2,3-dienyloxy)-1-naphthaldehyde (**1j**; Scheme 2). Hydroarylation and deformylation then occurred to yield benzochromene **3j**.

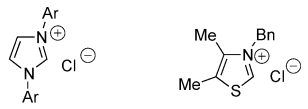
Though the exact mechanism is still not totally clear at present, some information has been gathered: 1) When the reaction of **1a** was conducted at 150 °C in the absence of DBU the putative intermediate 3-(buta-1,3-dien-2-yl)-2-hydroxybenzaldehyde (**4a**) was isolated in an appreciable amount (Scheme 1). 2) When allenic Claisen-type rearrangement adduct **4a** was heated with DBU at 150 °C in a sealed tube, only chromene **3a** was formed. These results suggested that formation of chromenes **3** is strictly a formal hydroarylation process divided into two parts, namely, allenic Claisen-type rearrangement and subsequent oxycyclization reaction.

Next, the general reactivity of 2-(propa-1,2-dienyloxy)benzaldehydes **5** toward the intramolecular hydroacylation reaction was tested. Allenal **5a** was synthesized from 2-(prop-2-ynyloxy)benzaldehyde according to a literature procedure.[9] Novel allenals **5b–e** and **5g** were prepared by using the above standard procedure with slight modifications (Scheme 3). Allenal **5f** was directly prepared in modest yield from 4-(diethylamino)-2-(prop-2-ynyloxy)benzaldehyde through treatment with base (Scheme 3).



Scheme 3. Preparation of 2-(propa-1,2-dienyloxy)benzaldehydes **5a–g**.

In the model hydroacylation reaction, we tested the behavior of **5a** using different conditions. The reactivity of substrate **5a** was screened by the use of commercially available imidazolium salt **6** as well as readily prepared thiazolium chloride **7** (Figure 1).[10] The combination of an amine base and azolium salts **6** or **7** should produce the necessary nucleophilic zwitterionic catalyst in situ, which promotes the allenal to chromone conversion.[11] With these precatalysts in hand, we next con-



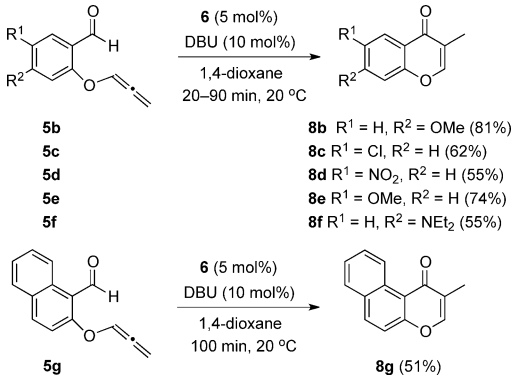
6 Ar = 2,4,6-MeC_6H_2 **7**

Figure 1. Structure of azolium salt precatalysts **6** and **7**.

ducted the optimization of the reaction conditions by scrutinizing the nature of the base, the molar ratio of the catalyst, and the solvent.

Initially, the reaction of 2-(propa-1,2-dienyloxy)benzaldehyde (**5a**) was carried out by using different loading (1–10 mol%) of both azolium precatalysts and bases. The activity of the azolium salt precatalyst highly affected this reaction, because superior yields were obtained by the use of imidazolium salt **6** in comparison with thiazolium chloride **7** (Table 1, entries 1 and 2). Among the bases surveyed, DBU was found to be the most effective to generate the desired chromone **8a** in good chemical yield. Other bases such as K_2CO_3 or triethylamine afforded poor (thiazolium chloride **7**) or moderate (imidazolium chloride **6**) yields of chromone **8a** (Table 1, entries 2–4). Optimization of the solvent revealed that 1,4-dioxane was superior to THF, CH_3CN, CH_2Cl_2, or toluene (Table 1, entries 4, 6–9). The optimal amount of catalyst was established at 5 mol% with an azolium salt/base ratio of 1:2. A lower loading of catalyst had the effect of lowering the conversion for a fixed reaction time (Table 1, entry 5). The same tendency was also observed when the quantity of base was decreased. Optimal reactivity was obtained at room temperature when 5 mol% of imidazolium chloride **6** and 10 mol% of DBU were employed in 1,4-dioxane (Table 1, entry 4).

With the best chromone-formation conditions identified, the scope of this transformation was then examined. The scope of the optimized reaction was demonstrated by utilizing varied 2-(propa-1,2-dienyloxy)-derived benzaldehydes **5b**–**g**. As shown in Scheme 4, various substituents with different electronic features on the phenyl ring showed good reactivity irrespective of the position. Both, aryl allenals **5b**,**e**,**f** bearing electron-donating substituents (MeO and Et_2N) and aryl allenals **5c**,**d** with electron-withdrawing substituents (Cl, NO_2) worked well to afford the corresponding 3-methylchromone **8b**–**f**. Pleasingly, a reasonable yield of tricyclic chromone **8g** was obtained for allenal **5g** despite the steric demand next to the carbaldehyde function.



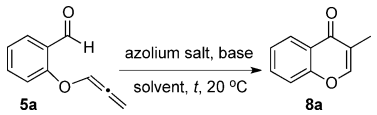
Scheme 4. NHC-catalyzed intramolecular hydroacylation reaction of allenals **5a**–**g**.

It was interesting to extend the same methodology to starting allenals bearing either a nonterminal allene moiety or an allene with an N atom as the linker in place of an O atom. Unfortunately, as shown in Scheme 5, efforts for the obtention of such allenals were in vain. The transformation of *N*-(2-formylphenyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide or *N*-[2-(dimethoxymethyl)phenyl]-4-methyl-*N*-(propa-1,2-dienyl)benzenesulfonamide into the N-tethered *N*-(2-formylphenyl)-4-methyl-*N*-(propa-1,2-dienyl)benzenesulfonamide using either the standard procedure used in Scheme 3 or a direct one-pot procedure was unsuccessful. In addition, the NHC-catalyzed reaction of the *N*-allenyl acetal did not work (Scheme 5). Similarly, 1-(dimethoxymethyl)-2-(3-phenylprop-2-ynyloxy)benzene could not be transformed into the corresponding nonterminal allenal.

A conceivable mechanism for the formation of chromones **8** from 2-(propa-1,2-dienyloxy)-derived benzaldehydes **5** is shown in Scheme 6. It may initially involve the nucleophilic addition of a zwitterionic species **9**, generated in situ from the exposure of imidazolium salt **6** to DBU, to an allene carbaldehyde **5**. This addition product, alkoxide **10**, initiates a 1,2-hydrogen-group migration and produces intermediate **11**. Species **11** would suffer a regioselective carbocyclization through intramolecular attack of the carbanion to the central carbon of the allenol ether, to afford intermediate **12**. The formation of species **12** could trigger a 1,3-proton shift, thus leading to zwitterionic species **13**, which, after re-formation of the carbonyl group, would produce chromones **8** with concurrent regeneration of the catalyst.

The above-mentioned mechanistic proposal was analyzed with the help of density functional theory

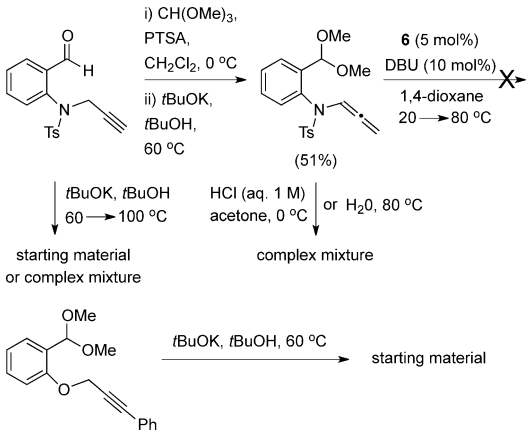
Table 1. Selective hydroacylation reaction of allenal **5a** under modified NHC-catalyzed conditions.



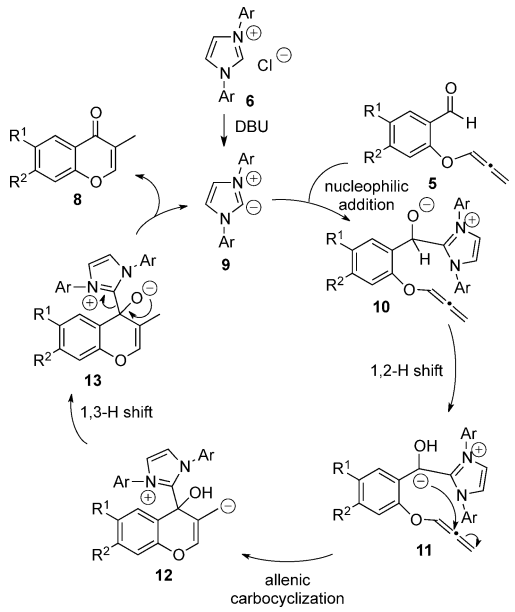
5a **8a**

Entry	Base ([mol%])	Azolium salt ([%])	Solvent/*t* [h]	Yield [%][a]
1	DBU (10)	**7** (5)	1,4-dioxane/20	20
2	Et_3N (10)	**6** (5)	1,4-dioxane/6	56
3	K_2CO_3 (10)	**6** (5)	1,4-dioxane/6	62
4	DBU (10)	**6** (5)	1,4-dioxane/0.5	85
5	DBU (4)	**6** (2)	1,4-dioxane/14	10
6	DBU (10)	**6** (5)	toluene/2	57
7	DBU (10)	**6** (5)	CH_2Cl_2/1.5	60
8	DBU (10)	**6** (5)	CH_3CN/1	64
9	DBU (10)	**6** (5)	THF/0.8	69

[a] Yield of pure, isolated product with correct analytical and spectral data.



Scheme 5. Non-productive preparation of N-tethered or nonterminal allenals.



Scheme 6. Rationalization for the NHC-catalyzed intramolecular hydroacylation reaction of allenals **5**.

(DFT) calculations. To this end, the reaction profile between allene carbaldehyde **5a** and the model NHC catalyst **6M** (in which the aryl groups attached to the nitrogen atoms were replaced by methyl groups) was computed at the PCM-M06-2X/6-311+G(d)//B3LYP/6-31+G(d) level.[12]

As readily seen in Figure 2, which gathers the corresponding free energies (at 298 K) in 1,4-dioxane solution, the process begins with the slightly endergonic formation of zwitterionic intermediate **INT1** ($\Delta G_{298} = 2.8$ kcal mol^{-1}). This process occurs through the transition state **TS1**, a saddle point associated with the nucleophilic addition of the NHC to the aldehyde moiety of **5a**, thus forming the new C–C bond (computed activation barrier of 12.6 kcal mol^{-1}). Then, **INT1** is transformed into its less stable isomer **INT2** through a 1,2-hydrogen shift (very likely assisted by solvent). From **INT2**, a regioselective ring-closure reaction takes place leading to **INT3** in an exergonic transformation ($\Delta G_{298} = -8.3$ kcal mol^{-1}). Both the exergonicity and regioselectivity of this step are directly related to the stabilization of the negative charge in zwitterion **INT3** due to allylic conjugation. As seen in Figure 2, this transformation occurs via **TS2**, which is associated with the nucleophilic attack of the carbanionic center of **INT2** at the central carbon of the allene moiety (activation barrier of 9.7 kcal mol^{-1}). Once zwitterionic intermediate **INT3** is formed, an intramolecular 1,3-hydrogen shift occurs to produce **INT4** in a highly exergonic transformation ($\Delta G_{298} = -34.2$ kcal mol^{-1}). Finally, the process ends up with the dissociation of the NHC catalyst thus forming the experimentally observed chromone **8a**. The ease of this final step becomes evident from the high exergonicity ($\Delta G_{298} = -19.9$ kcal mol^{-1}) and very low activation barrier ($\Delta G^{\neq} = 0.8$ kcal mol^{-1}) computed for this process.

From the above-computed reaction profile, it is clear that the origin of the observed divergent reactivity between the initial allenes **1** and **5** should be related to the ring-closure step involving **TS2**. Indeed, our calculations indicate that the activation barrier associated with **INT2′** (derived from **1a**)→**TS2′**→**INT3′** is 20.7 kcal mol^{-1}, which is 11 kcal mol^{-1} higher than analogous processes involving **TS2**. In addition, the process is endergonic ($\Delta G_{298} = 3.1$ kcal mol^{-1}), which is in contrast to the exergonicity computed for the formation of the analogous six-

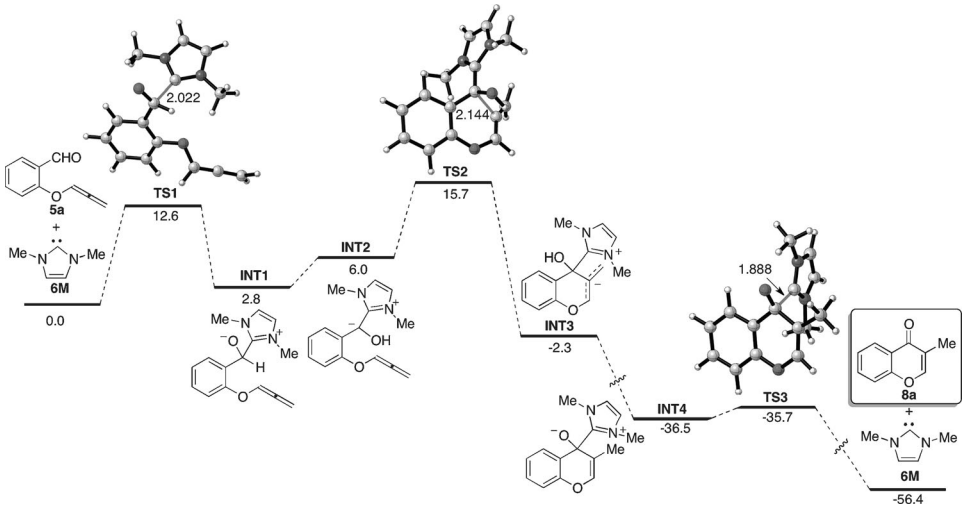


Figure 2. Computed reaction profile for the reaction of allene carbaldehyde **1a** and 1,3-bis(methyl)-1,3-dihydro-2*H*-imidazol-2-ylidene catalyst to produce chromone **8a**. Relative free energies (ΔG, at 298 K) are given in kcal mol^{-1} and bond lengths in the transition states in angstroms. All data have been computed at the PCM(1,4-dioxane)-M06-2X/6-311+G(d)//B3LYP/6-31+G(d) level.

membered ring **INT3** (see above). Moreover, the computed activation barrier is even higher ($\Delta G^{\neq} = 26.4$ kcal mol^{-1}) and the process more endergonic ($\Delta G_{298} = 7.3$ kcal mol^{-1}) when using the more realistic NHC catalyst bearing two phenyl rings attached to the nitrogen atoms (Figure 3). Therefore, our calculations suggest that the formation of the zwitterionic seven-membered ring **INT3′** is not favored.

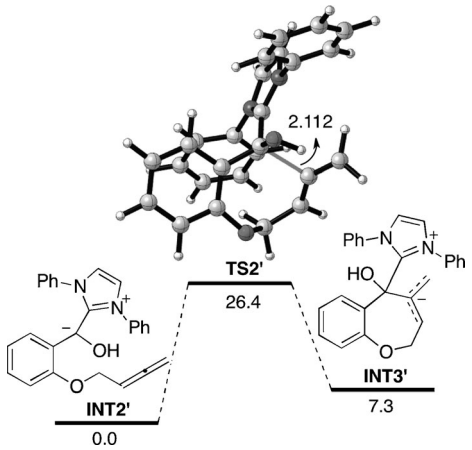


Figure 3. Computed **INT2′** to **INT3′** transformation. See Figure 2 for additional caption details.

Inspection of the molecular orbitals responsible for the ring closure provides a reasonable explanation for this differential behavior. As seen in Figure 4, the HOMO of **INT2** (derived from **5a**) and **INT2′** (derived from **1a**) is quite similar, that is, it can be considered as a lone pair located on the carbon atom responsible for the nucleophilic attack to the allene moiety. Similarly, the LUMO of **INT2** and LUMO+1 of **INT2′** can be viewed as the electrophilic π^* molecular orbital (MO) involving the central carbon atom of the allene. Strikingly, the oxygen atom directly attached to the allene fragment in **INT2** leads to a significant stabilization of this π^* (MO) as compared to that in **INT2′** (Figure 4). As a result, a much lower HOMO–LUMO gap ($\Delta\Delta E = 0.4$ eV) is computed for **INT2**, which is translated into a much lower activation barrier.

Finally, we studied in detail the allenic Claisen rearrangement occurring in **1a**. As depicted in Figure 5, the transformation proceeds concertedly through the six-membered transition state **TS4** to afford intermediate **INT5**, which rapidly isomerizes to the experimentally observed reaction product **4a** in a highly exergonic transformation ($\Delta G_{298} = -19.2$ kcal mol^{-1}). Of course, the reestablishment of the aromaticity of the aryl fragment in **4a** constitutes the driving force of the transformation. Similar to related pericyclic reactions,[13] the associated transition state **TS4** can be considered as an aromatic transition state in view of the negative nucleus independent chemical shift (NICS)[14] values computed at the [3,+1] ring critical point of the electron density (NICS(0) = −16.4 ppm) and the corresponding out-of-plane tensor component computed 1 Å above (NICS(1)$_{zz}$ = −23.4 ppm). Similar NICS values were found in related Claisen rearrangements involving allenyl vinyl ethers.[15] The aromatic nature of **TS4** was further confirmed by

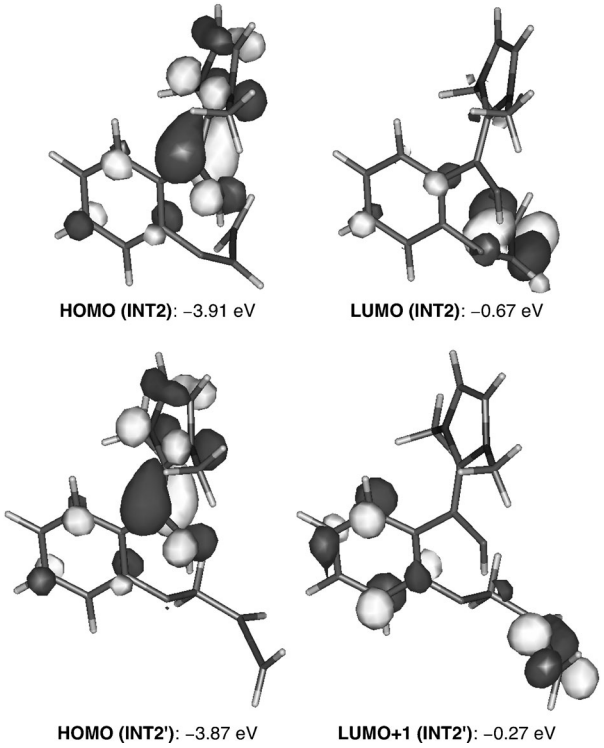


Figure 4. Computed molecular orbitals involved in the ring-closure step of intermediates **INT2** and **INT2′** (isosurface value of 0.05 a.u.).

the clear diatropic (i.e., aromatic) current present in this species as revealed by the anisotropy of the induced current density (ACID)[16] method (see the inset in Figure 5).

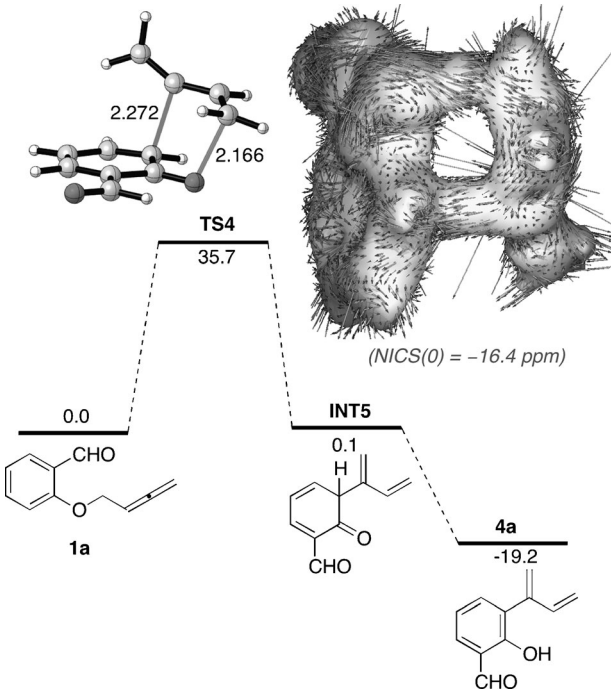


Figure 5. Computed profile for the allene Claisen rearrangement involving **1a**. Inset: ACID plot computed for **TS4** (isocontour value of 0.04 a.u.).

Conclusion

We report that 2-(buta-2,3-dienyloxy)benzaldehydes undergo a formal allenic hydroarylation reaction to afford chromenes, whereas 2-(propa-1,2-dienyloxy)benzaldehydes react to yield chromones. The formation of chromenes can be explained through a tandem allenic Claisen rearrangement/oxycyclization sequence, whereas a NHC-catalyzed allenic hydroacylation reaction must be invoked to account for the preparation of chromones. In addition, to understand this unanticipated difference in reactivity, a DFT study has been performed. Our calculations suggest that the origin of the observed differential reactivity is strongly related to the stabilization of the π^* molecular orbital involving the central carbon atom of the allene moiety in allene carbaldehydes **5**.

Experimental Section

Computational details

All the calculations reported in this paper were obtained with the Gaussian 09 suite of programs.[17] Electron correlation was partially taken into account by using the B3LYP[18] hybrid functional using the standard double-ζ quality plus polarization and diffuse functions 6-31+G(d) for all atoms. Reactants and products were characterized by frequency calculations,[19] and have positive definite Hessian matrices. Transition-state structures (TS's) show only one negative eigenvalue in their diagonalized force-constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the intrinsic reaction coordinate (IRC) method.[20] Solvent effects were taken into account by using the polarizable continuum model (PCM).[21] Single-point calculations on the gas-phase optimized geometries were performed to estimate the change in the Gibbs energies in the presence of 1,4-dioxane as solvent using the dispersion-corrected M06-2X[22] functional and the triple-ζ quality 6-311+G(d) basis sets. This level is denoted PCM(1,4-dioxane)-M06-2X/6-311+G(d)//B3LYP/6-31+G(d).

General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-300 or Varian VRX-300S spectrometer. NMR spectra were recorded for solutions in $CDCl_3$, except otherwise stated. Chemical shifts are given in ppm relative to tetramethylsilane (TMS; ^{1}H, 0.0 ppm) or $CDCl_3$ (^{13}C, 76.9 ppm). Low- and high-resolution mass spectra were recorded on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. All commercially available compounds were used without further purification.

General procedure for the microwave-promoted formal hydroarylation reaction of allenals 1: Preparation of chromenes 3

A stirred suspension of the corresponding 2-(buta-2,3-dienyloxy)-benzaldehyde **1** (0.5 mmol) in water (6.0 mL) was heated at 200 °C under microwave irradiation until disappearance of the starting material (by TLC). The reaction was allowed to cool to room temperature, before being extracted with ethyl acetate (3×5 mL). The organic phase was washed with brine (2×5 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate or dichloromethane/ethyl acetate mixtures gave analytically pure compounds **3**.[23]

Chromene 3a

Obtained from allenal **1a** (100 mg, 0.57 mmol). After chromatography of the residue using hexanes/dichloromethane (3:7) as eluent, compound **3a** (54 mg, 54%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 10.36 (d, J = 0.9 Hz, 1H), 7.57 (dd, J = 7.9, 1.6 Hz, 1H), 7.45 (dd, J = 7.4, 1.6 Hz, 1H), 7.00 (dt, J = 7.6, 0.7 Hz, 1H), 5.79 (m, 1H), 4.92 (m, 2H), 2.04 ppm (q, J = 1.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 189.0, 158.1, 135.8, 130.1, 129.9, 127.2, 126.2, 124.7, 121.7, 120.5, 66.7, 18.1 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2935, 1685, 1421, 1228 cm^{-1}; HRMS (ES): *m/z* calcd for $C_{11}H_{10}O_2$ $[M]^+$: 174.0681; found: 174.0676.

Chromene 3b

Obtained from allenal **1b** (110 mg, 0.53 mmol). After chromatography of the residue using hexanes/dichloromethane (1:2) as eluent, compound **3b** (48 mg, 44%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.33 (s, 1H), 7.61 (d, J = 2.6 Hz, 1H), 7.26 (d, J = 2.6 Hz, 1H), 5.72 (m, 1H), 4.92 (m, 2H), 2.03 ppm (q, J = 1.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 188.2, 155.7, 128.9, 128.7, 126.8, 126.5, 126.2, 124.6, 120.2, 66.2, 18.1 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 1683, 1413, 1228 cm^{-1}; HRMS (ES): *m/z* calcd for $C_{11}H_9ClO_2$ $[M]^+$: 208.0291; found: 208.0301.

Chromene 3c

Obtained from allenal **1c** (176 mg, 1.03 mmol). After chromatography of the residue using hexanes/dichloromethane (1:10) as eluent, compound **3c** (96 mg, 54%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 7.44 (d, J = 7.7 Hz, 2H), 7.03 (t, J = 7.7 Hz, 1H), 5.78 (m, 1H), 4.95 (m, 2H), 2.02 ppm (q, J = 1.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.5, 132.8, 129.3, 128.8, 125.5, 122.2, 121.1, 116.6, 100.7, 67.3, 17.8 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 1684, 1228 cm^{-1}; HRMS (ES): *m/z* calcd for $C_{11}H_9NO$ $[M]^+$: 171.0684; found: 171.0684.

Chromene 3d

Obtained from allenal **1d** (140 mg, 0.87 mmol). After chromatography of the residue using hexanes/dichloromethane (3:1) as eluent, compound **3d** (43 mg, 31%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.94 (m, 2H), 6.71 (d, J = 7.9 Hz, 1H), 5.58 (m, 1H), 4.71 (m, 2H), 2.29 (s, 3H), 2.02 ppm (q, J = 1.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 151.9, 130.3, 130,2, 129.3, 124.1, 124.0, 118.5, 115.4, 65.3, 20.8, 18.0 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2923, 1496, 749 cm^{-1}; HRMS (ES): *m/z* calcd for $C_{11}H_{12}O$ $[M]^+$: 160.0888; found: 160.0890.

Chromene 3e

Obtained from allenal **1e** (100 mg, 0.46 mmol). After chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent, compound **3e** (49 mg, 49%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 10.33 (s, 1H), 8.35 (d, J = 2.6 Hz, 1H), 8.14 (d, J = 2.8 Hz, 1H), 5.98 (m, 1H), 5.19 (m, 2H), 2.14 ppm (q, J = 1.8 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 187.7, 162.5, 140.0, 128.4, 126.8, 124.3, 123.6, 123.1, 122.6, 68.3, 18.0 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 1688, 1338, 1242 cm^{-1}; HRMS (ES): *m/z* calcd for $C_{11}H_9NO_4$ $[M]^+$: 219.0532; found: 219.0524.

Chromene 3 f

Obtained from allenal **1 f** (170 mg, 0.89 mmol). After chromatography of the residue using hexanes/ethyl acetate (12:1) as eluent, compound **3 f** (75 mg, 44%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 8.04 (dd, J = 8.8, 2.6 Hz, 1H), 7.97 (d, J = 2.8 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H) 5.83 (m, 1H), 4.96 (m, 2H), 2.08 ppm (q, J = 1.9 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 160.7, 128.9, 126.5, 125.9, 124.7, 121.7, 119.8, 116.8, 116.0, 67.4, 17.8 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2936, 1490, 1220, 750 cm^{-1}; HRMS (ES): m/z calcd for $C_{10}H_9NO_3$ $[M]^+$: 191.0582; found: 191.0590.

Chromene 3 g

Obtained from allenal **1 g** (200 mg, 1.37 mmol). After chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, compound **3 g** (80 mg, 40%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.14 (m, 2H), 6.92 (m, 2H), 6.81 (m, 1H), 5.59 (m, 1H), 4.76 (m, 2H), 2.29 (s, 3H), 2.04 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.1, 130.2, 128.9, 124.3, 123.5, 121.1, 118.3, 115.7, 65.4, 17.9 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 3038, 1485, 1450, 1220, 750 cm^{-1}; HRMS (ES): m/z calcd for $C_{10}H_{10}O$ $[M]^+$: 146.0732; found: 146.0729.

Chromene 3 h

Obtained from allenal **1 h** (180 mg, 0.95 mmol). After chromatography of the residue using hexanes/ethyl acetate (15:1) as eluent, compound **3 h** (79 mg, 44%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.59 (dd, J = 7.9, 1.7 Hz, 1H), 7.29 (dd, J = 7.6, 1.8 Hz, 1H), 6.94 (m, 1H), 5.66 (m, 1H), 4.84 (m, 2H), 2.61 (s, 3H), 2.04 ppm (q, J = 1.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 199.5, 154.0, 130.0, 129.5, 127.5, 126.9, 125.1, 120.7, 118.5, 65.4, 31.8, 18.3 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2926, 1672, 742 cm^{-1}; HRMS (ES): m/z calcd for $C_{12}H_{12}O_2$ $[M]^+$: 188.0837; found: 188.0829.

Chromene 3 i

Obtained from allenal **1 i** (150 mg, 0.73 mmol). After chromatography of the residue using hexanes/ethyl acetate (15:1) as eluent, compound **3 i** (78 mg, 52%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 10.22 (d, J = 0.8 Hz, 1H), 7.64 (d, J = 8.9 Hz, 1H), 6.76 (d, J = 8.8 Hz, 1H), 5.69 (m, 1H), 4.64 (m, 2H), 3.93 (s, 3H), 2.16 ppm (q, J = 1.6 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 187.9, 162.8, 160.2, 131.3, 129.0, 119.9, 119.5, 116.7, 106.3, 65.8, 56.3, 22.0 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2927, 1656, 1459, 1322 cm^{-1}; HRMS (ES): m/z calcd for $C_{12}H_{12}O_3$ $[M]^+$: 204.0786; found: 204.0785.

Chromene 3 j

Obtained from allenal **1 j** (150 mg, 0.67 mmol). After chromatography of the residue using hexanes/ethyl acetate (23:1) as eluent, compound **3 j** (76 mg, 58%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): δ = 8.15 (d, J = 8.6 Hz, 1H), 7.83 (m, 1H), 7.75 (m, 1H), 7.47 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.35 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.13 (d, J = 8.9 Hz, 1H), 5.81 (m, 1H), 4.52 (m, 2H), 2.38 ppm (q, J = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 25 °C): δ = 155.0, 133.0, 131.6, 131.3, 130.9, 129.7, 126.9, 124.1, 120.2, 119.3, 118.5, 64.9, 22.6 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 1232, 750 cm^{-1}; HRMS (ES): m/z calcd for $C_{14}H_{12}O$ $[M]^+$: 196.0888; found: 196.0879.

General procedure for the NHC-catalyzed hydroacylation reaction of allenals 5: Preparation of chromones 8

DBU (15 mg, 0.10 mmol, 15 μL) was added at room temperature to a stirred solution of imidazolium chloride **6** (0.05 mmol) in 1,4-dioxane (2 mL). After 10 min, the appropriate 2-(propa-1,2-dienyloxy)-benzaldehyde **5** (1.0 mmol) in 1,4-dioxane (1 mL) was added. The reaction mixture was stirred until complete disappearance (by TLC) of the starting material and filtered through a pack of Celite. The filtrate was extracted with ethyl acetate (3×5 mL), and the combined extracts were washed twice with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure, and analytically pure adducts **8** were obtained after purification by flash chromatography on silica gel using hexanes/ethyl acetate mixtures.

Chromone 8 a

Obtained from allenal **5 a** (100 mg, 0.62 mmol). After chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, compound **8 a** (85 mg, 85%) was obtained as a pale brown solid. M.p. 70–71 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.22 (dd, J = 1.7, 7.9 Hz, 1H), 7.78 (d, J = 1.0 Hz, 1H), 7.62 (ddd, J = 1.6, 7.0, 8.5 Hz, 1H), 7.37 (m, 2H), 2.02 ppm (d, J = 1.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 178.2, 156.6, 151.7, 133.2, 125.7, 124.7, 123.5, 120.6, 117.9, 11.1 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1641, 1467 cm^{-1}; HRMS (ES): m/z calcd for $C_{10}H_8O_2$ $[M]^+$: 160.0524; found: 160.0524.

Chromone 8 b

Obtained from allenal **5 b** (31 mg, 0.17 mmol). After chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent, compound **8 b** (25 mg, 81%) was obtained as a pale brown solid. M.p. 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.12 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 1.2 Hz, 1H), 6.94 (dd, J = 2.3, 8.9 Hz, 1H), 6.79 (d, J = 2.3 Hz, 2H), 3.88 (s, 3H), 2.01 ppm (d, J = 1.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 177.7, 163.7, 158.8, 151.2, 127.1, 120.5, 117.6, 114.2, 99.9, 55.7, 11.1 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2964, 1639, 1607 1440 cm^{-1}; HRMS (ES): m/z calcd for $C_{11}H_{10}O_3$ $[M]^+$: 190.0630; found: 190.0623.

Chromone 8 c

Obtained from allenal **5 c** (42 mg, 0.22 mmol). After chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, compound **8 c** (26 mg, 62%) was obtained as a colorless solid. M.p. 96–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.18 (d, J = 2.6 Hz, 1H), 7.80 (br s, 1H), 7.58 (dd, J = 8.9, 2.6 Hz, 1H), 7.38 (d, J = 8.9 Hz, 1H), 2.03 ppm (br s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 177.1, 154.9, 151.9, 133.5, 130.7, 125.1, 124.4, 120.9, 119.8, 11.1 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 1639, 1611, 1486 cm^{-1}; HRMS (ES): m/z calcd for $C_{10}H_7ClO_2$ $[M]^+$: 194.0135; found: 194.0128.

Chromone 8 d

Obtained from allenal **5 d** (76 mg, 0.35 mmol). After chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, compound **8 d** (42 mg, 55%) was obtained as a pale brown solid. M.p. 145–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.11 (d, J = 2.7 Hz, 1H), 8.48 (dd, J = 2.8, 9.2 Hz, 1H), 7.86 (d, J = 1.3 Hz, 1H), 7.59 (d, J = 9.2 Hz, 1H), 2.08 ppm (d, J = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 176.8, 159.4, 151.9, 144.5, 127.6, 123.5, 122.7, 121.8, 119.8, 11.1 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2973, 2926, 1639, 1600 cm^{-1}; HRMS (ES): m/z calcd for $C_{10}H_7NO_4$ $[M]^+$: 205.0375; found: 205.0381.

Chromone 8e

Obtained from allenal **5e** (54 mg, 0.26 mmol). After chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, compound **8e** (40 mg, 74%) was obtained as a colorless solid. M.p. 74–76 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.78 (d, J = 1.2 Hz, 1H), 7.58 (d, J = 3.1 Hz, 2H), 7.35 (d, J = 9.1 Hz, 2H), 7.23 (dd, J = 9.2, 3.1 Hz, 1H), 3.89 (s, 3H), 2.04 ppm (d, J = 1.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 178.1, 156.6, 151.6, 151.5, 124.1, 123.4, 119.8, 119.4, 104.7, 55.8, 11.2 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 1639, 1611, 1486 cm^{-1}; HRMS (ES): *m/z* calcd for $C_{11}H_{10}O_3$ $[M]^+$: 190.0630; found: 190.0625.

Chromone 8f

Obtained from allenal **5f** (30 mg, 0.15 mmol). After chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, compound **8f** (16 mg, 55%) was obtained as a pale brown solid. M.p. 100–102 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.03 (d, J = 9.0 Hz, 1H), 7.61 (d, J = 1.2 Hz, 1H), 6.73 (dd, J = 2.5, 9.2 Hz, 1H), 6.43 (br s, 1H), 3.43 (q, J = 7.1 Hz, 4H), 1.98 (d, J = 1.1 Hz, 3H), 1.22 ppm (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 177.4, 159.1, 158.8, 151.3, 150.4, 126.9, 119.8, 110.5, 96.4, 44.8 (2C), 12.4 (2C), 11.2 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1643, 1529, 1380 cm^{-1}; HRMS (ES): *m/z* calcd for $C_{14}H_{17}NO_2$ $[M]^+$: 231.1259; found: 231.1257.

Chromone 8g

Obtained from allenal **5g** (39 mg, 0.19 mmol). After chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, compound **8g** (20 mg, 51%) was obtained as a colorless solid. M.p. 71–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.11 (dd, J = 8.6, 0.5 Hz, 1H), 8.06 (d, J = 9.0 Hz, 1H) 7.91 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 1.2 Hz, 1H), 7.77 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.62 (ddd, J = 8.0, 7.0, 1.2 Hz, 1H), 7.49 (d, J = 9.1 Hz, 1H), 2.13 ppm (d, J = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 180.0, 157.9, 149.3, 135.1, 130.7, 130.5, 129.2, 128.1, 127.1, 126.4, 123.5, 117.7, 116.7, 11.6 ppm; IR ($CHCl_3$): $\tilde{\nu}$ = 2924, 1648, 1620, 1551, 1443 cm^{-1}; HRMS (ES): *m/z* calcd for $C_{14}H_{10}O_2$ $[M]^+$: 210.0681; found: 210.0681.

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[23] Experimental procedures as well as full spectroscopic and analytical data for compounds not included in this Experimental Section are described in the Supporting Information. It contains compound characterization data, experimental procedures, Cartesian coordinates, and copies of NMR spectra for all new compounds.

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FULL PAPER

Synthetic Methods

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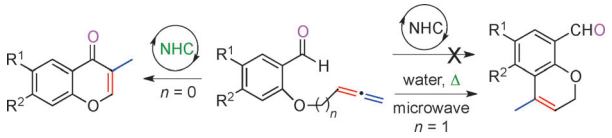
Divergent Reactivity of Homologue *ortho*-Allenylbenzaldehydes Controlled by the Tether Length: Chromone versus Chromene Formation



Separate ways: The divergent behavior of two homologue allenals as cyclization substrates is described. 2-(Buta-2,3-dienyloxy)benzaldehydes suffered a formal allenic hydroarylation reaction to afford chromenes, whereas 2-(propa-1,2-dienyloxy)benzaldehydes reacted to yield chromones by means of NHC-catalyzed allenic hydroacylation (see scheme). To understand this unanticipated difference in reactivity, a DFT study has been performed.