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Insights into the Morita-Baylis-Hillman reaction of Isomeric Dibenzofuran Carbaldehydes: A Theoretical and Mass spectral Study

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We herein report a faster Morita-Baylis-Hillman (MBH) reaction of dibenzofuran-4-carbaldehyde (**2**) over its isomer, dibenzofuran-2-carbaldehyde (**1**) with different activated olefins in the presence of DABCO as base catalyst. We observed that there is no significant effect of solvent (methanol) on the reation rates. In situ mass spectrometry experiments and computational studies were applied to understand the role of reaction intermediates and their structure implications. MS data revealed that the zwitterionic intermediate obtained from **2** is more stable than that obtained from **1**. Computational studies were performed on the gas as well as solvent phase reactions at mPW1K/6-31+G(d,p) level. In accordance with the experimental results aldehyde **2** is found to be more reactive compared to **1**. The results are in accordance with the McQuade's proposal of MBH mechanism where the second equivalent of aldehyde plays a key role in proton migration step during the course of reaction in the absence of methanol solvent.

Introduction

Morita-Baylis-Hillman (MBH) reaction[1] is one of the most powerful leading named reactions in organic synthesis for the construction of C-C bond.[2] It is synthetically equivalent to the addition of a vinyl anion to an electrophile (carbonyl compound) in presence of a tertiary amine as the base catalyst. Contributions to the development of MBH reaction enhanced in several folds by modifying electrophiles, activated olefin or catalyst.[3] Despite plethora of reports on the application of MBH adducts, the general sluggishness of reaction continued to be a prime concern. The key drawback that still holds on MBH reaction is its poor reaction rate. The attempted methods using ultrasound,[4] microwave,[5] molten salts,[6] ionic liquids,[7] organo catalysis[8] and other advanced techniques did not help much in improving the rate of the reaction. All these observations have prompted worldwide researchers to attempt number of mechanistic investigations[9] to reduce the reaction time.

Although, the studies involving correlation of theoretical and experimental investigations provide some insights into the reaction, there are many questions to be answered. Way to enhance rate of this reaction is still a puzzle to be solved. The best known faster MBH reactions are with heterocyclic aldehydes. The reaction between substituted 2-chloronicotinic aldehydes[10] and methyl acrylate or acrylonitrile was completed within 15 min. Similar reaction time was also observed in the case of 3-aryl-5-isoxazolecarboxaldehyde (Figure 1).[11,12] In view of such significant observations, we examined the positional and steric effects of formyl group on MBH reaction with isomeric dibenzofuran aldehydes.

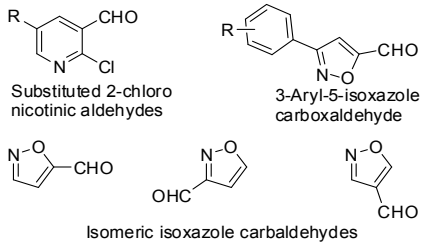

Figure 1. Heterocyclic aldehydes previously used as substrates in Baylis-Hillman reaction.

We herein report our results on remarkable difference in the rates of MBH reactions of isomeric dibenzofuran aldehydes, i.e., dibenzofuran-2-carbaldehyde (**1**) and dibenzofuran-4-carbaldehyde (**2**) with activated olefins in presence of a base catalyst. The mechanistic aspects of the rate of MBH reaction with aldehydes **1** and **2** were examined by using high resolution electrospray ionization-mass spectrometry (ESI-MS), tandem mass spectrometry (MS/MS) and computational studies.

Results and discussion

To begin with, the required dibenzofuran-2-carbaldehyde (**1**) was synthesized from dibenzofuran using the procedure developed in our lab.[13] Dibenzofuran-4-carbaldehyde (**2**) was prepared in 60% yield by reacting dibenzofuran with *n*-butyllithium/ dimethylformamide at -78°C. Both aldehydes **1**

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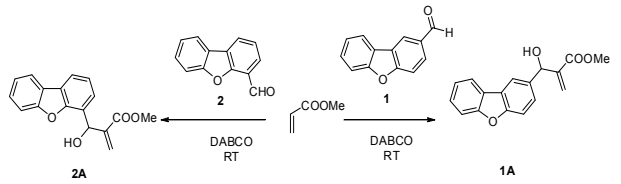
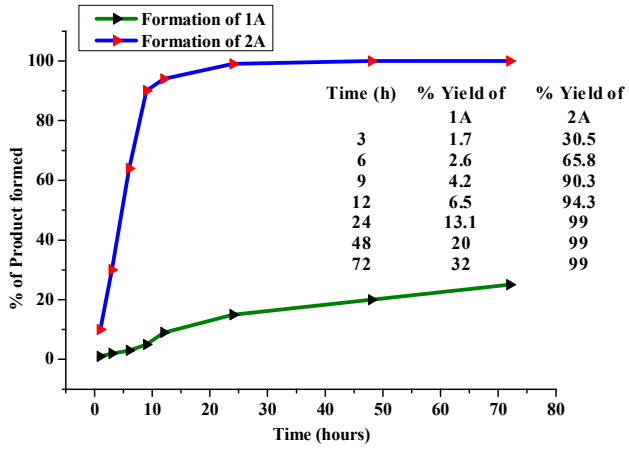
and **2** were characterized using NMR and mass spectral data and were correlated with literature.[13,14]



Scheme 1. MBH reaction of isomeric aldehydes 1 and 2 with methyl acrylate.

Initiating the study, we performed Morita-Baylis-Hillman (MBH) reaction of aldehydes **1** and **2** with methyl acrylate in the presence of DABCO as a base catalyst (Scheme 1) at room temperature. The reaction with aldehyde **1** took seven days to yield MBH adduct **1A** in 75% yield. But when the same reaction performed with the isomeric aldehyde **2** under identical reaction conditions, surprisingly, it proceeded to complete conversion within 24 h to give MBH adduct **2A** in 99% yield. The products **1A** and **2A** were fully characterized by the ^{1}H, ^{13}C NMR and mass spectral data.

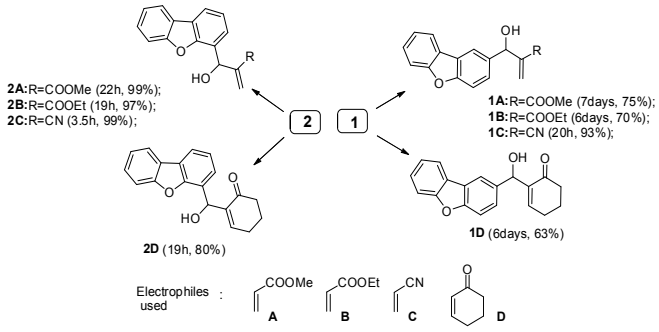


Time (h)	% Yield of 1A	% Yield of 2A
3	1.7	30.5
6	2.6	65.8
9	4.2	90.3
12	6.5	94.3
24	13.1	99
48	20	99
72	32	99

Figure 2. Percentage of formation of MBH adducts **1A** and **2A** from the respective reactions of isomeric aldehydes 1 and 2 with methyl acrylate at different time intervals analyzed by HPLC.

Further, we performed a systematic HPLC analysis of the reaction of aldehydes **1** and **2** with methyl acrylate at different reaction time points. The reaction mixtures drawn at different time intervals (3, 6, 9, 12, 24, 48 and 72 h) were analyzed by HPLC and calculated the percentage of MBH adducts **1A** and **2A** formed (Figure 2). Correlation of % product yields with reaction time revealed that the MBH reaction between aldehyde **2** and methyl acrylate was completed within 24 h to produce adduct **2A**, whereas at this reaction time only 13% adduct **1A** was formed with aldehyde **1** (Figure 2). These results clearly revealed that the MBH reaction of aldehyde **1** was much slower than that of isomeric aldehyde **2**.

Effect of electrophile: In order to get further insight, we next examined the MBH reaction with various electrophiles. The isomeric aldehydes **1** and **2** were thus reacted with different electrophiles such as methyl acrylate, ethyl acrylate, acrylonitrile and 2-cyclohexenone in presence of the base, DABCO (Scheme 2) under identical reaction conditions.



Scheme 2. MBH reaction of isomeric aldehydes **1** and **2** with various activated olefins **A-D**. The reaction time and yield were shown in parenthesis.

All the reactions produced corresponding MBH adducts **1A-D** and **2A-D** from the respective isomeric aldehydes **1** and **2**; but their yields were varied with the reaction time. The maximum yield of MBH adducts **1A-D** and **2A-D** with respect to reaction time is presented in Figure 3. All the MBH adducts **1A-D** and **2A-D** was fully characterized by their ^{1}H, ^{13}C NMR and mass spectral data.

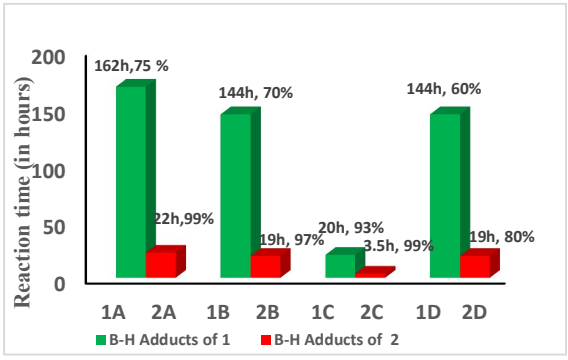
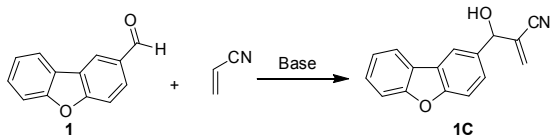


Figure 3. Graphical representation of the maximum yield of MBH adducts **1A-D** and **2A-D** and the reaction times [Aldehyde **1** or **2** (1 mmol), activated olefin (8 mmol) and DABCO (1 mmol) were stirred at room temperature].

The above experimental results (Figure 3) revealed that the MBH reactions with aldehyde **2** were completed in shorter reaction times when compared to the reactions with its isomeric aldehyde **1**. Among the four electrophiles, the reaction with acrylonitrile was faster when compared to the reactions with other three olefins (Figure 3). We also observed that all the reactions proceeded with six folds faster rate for aldehyde **2** when compared to that of aldehyde **1**. It suggests that the differences in the rate of reaction times were maintained almost same for both the isomeric aldehydes, irrespective of the electrophile used.

Effect of base and solvent: With a view to verifying the effect of the catalyst (base) on the MBH reaction, we have performed the reaction in the presence of different bases. We have chosen the reaction of aldehyde **1** with acrylonitrile for this study to enable monitoring the effect of base. The MBH reaction

(Scheme 3) was performed using different bases such as DBU, Quinuclidine, Et_3N, Imidazole, K_2CO_3, PPh_3 and DMAP. Among all the bases screened, the DABCO was found to be the effective base with good yield (93%) (Table 1). This suggests key role of DABCO in the differential rates of MBH reaction of the isomeric aldehydes. Further, the reaction of aldehyde **1** with acrylonitrile in methanol in the presence DABCO did not show any significant improvement in rate of BH reaction compared to the blank (without solvent) reaction.



Scheme 3. MBH reaction of aldehyde **1** with acrylonitrile and different bases.

Table 1. Effect of base on the MBH reaction of aldehyde **1** depicted in **Scheme-3**.

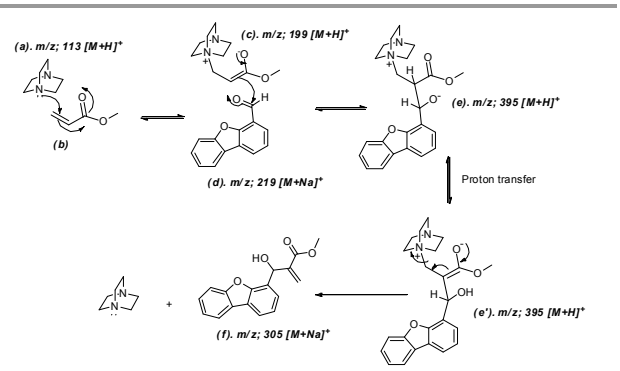
S.No.	Base	Yield (%)[a]
1	DABCO	93
2	DBU	<25
3	Et_3N	n.r.[b]
4	K_2CO_3	n.r.[b]
5	DMAP	<20
6	PPh_3	<10
7	Imidazole	n.r[b]
8	Quinuclidine	23

[a]All the reactions were performed at room temperature and yields were reported at 22h. [b]n.r. = No reaction was observed.

Mechanistic studies using In-situ ESI-MS analysis: Over the past decade, ESI-MS became an important tool[15] in mechanistic studies because of soft ionization process in ESI-MS and it also produces intact molecule ions directly from the solution phase. In the present study, we have used ESI-MS to investigate the reaction mechanism of MBH reaction of isomeric dibenzofuran aldehydes. Tandem mass spectrometry (MS/MS) and high resolution mass spectrometry (HRMS) techniques were used for characterization of key reaction intermediates. Based on the results discussed in the previous sections, we have selected the MBH reaction of the isomeric aldehydes **1** and **2** with methyl acrylate in the presence of DABCO for detailed mass spectral analysis.

According to wide accepted mechanism (Scheme 4), the first reaction step consists of the 1,4-addition of the catalytic tertiary amine (DABCO) (a) to the activated alkene (methyl acrylate) (b), which generates a zwitterionic intermediate (c). The next step involves the aldolic addition of zwitterion and aldehyde (d) to yield an intermediate (e). Later the intermediate (e) undergoes an intramolecular prototropic shift to form another intermediate (e'), which is isomeric to (e). In the last step the intermediate (e') forms the final MBH adduct (f) by releasing the intact base back in the solution.

For ESI-MS experiments, aldehyde **1** or **2** (1 equivalent), methyl acrylate (8 equivalent) and DABCO (1 equivalent) were mixed without additional solvent and allowed to react. The positive ion ESI mass spectra were recorded for the reaction



Scheme 4. Proposed reaction pathway for the MBH reaction of aldehyde **2** with methyl acrylate in the presence of DABCO.

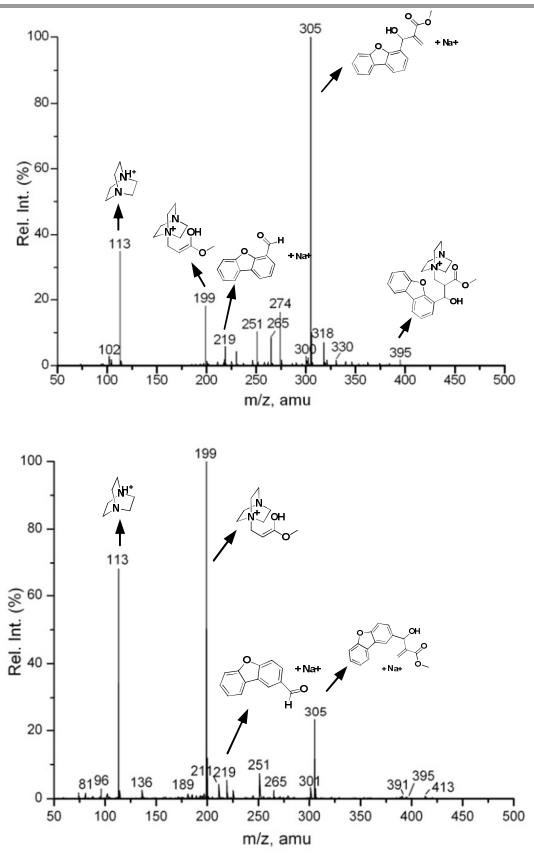


Figure 4. Positive ion ESI mass spectra of the reaction mixture of aldehyde **2** (Top) and aldehyde **1** (Bottom) after 3 hours.

mixtures at different reaction times (0.25, 3, 6, 9, 12 and 24 hours for aldehyde **2**, and 1, 3, 6, 9, 12, 24 and 48 hours for aldehyde **1**). The mass spectra included the peaks corresponding to the starting materials, i.e., $[M+H]^+$ ion of DABCO (a) at *m/z* 113 and $[M+Na]^+$ ion of dibenzofuran aldehyde (d) at *m/z* 219. The peak corresponding to methyl acrylate (b) could not be seen in the spectra, may be because it was not amenable to ionize under positive ion ESI conditions. The peak due to expected product was observed at *m/z* 305 (f),

which corresponds to $[M+Na]^+$ ion. The intermediate species appeared at *m/z* 199 (c) and 395 (e or e') (Figure 4).

Table 2. ESI-HRMS data of the ions detected in the reaction of aldehyde **2** at 3 hours (Similar data is obtained for aldehyde **1**; data not provided).

Observed *m/z*	Ion	Chemical Formula	Theoretical *m/z*	Error (in ppm)
113.1080	$[M+H]^+$	$C_6H_{13}N_2$	113.1078	1.1
199.1456	$[M+H]^+$	$C_{10}H_{19}N_2O_2$	199.1446	4.8
219.0418	$[M+Na]^+$	$C_{13}H_8O_2Na$	219.0421	-1.8
305.0801	$[M+Na]^+$	$C_{17}H_{14}O_4Na$	305.0789	3.7
395.1990	$[M+H]^+$	$C_{23}H_{27}N_2O_4$	395.1971	4.9

Though both the isomeric dibenzofuran aldehydes **1** and **2** showed similar set of ions, consistent differences were found in the ion yields of the reaction intermediates/products, i.e., the ions appearing at *m/z* 199 (c), 305 (f) and 395 (e). The ion yields of these ions were plotted against the reaction time point of the two reactions (Figure 5 and 6).

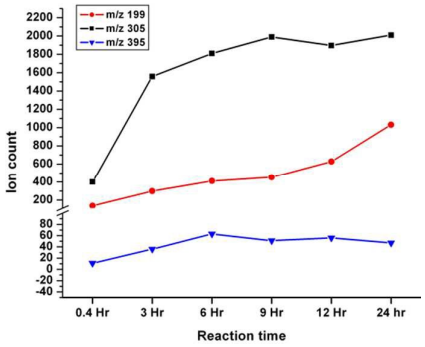


Figure 5. Ion counts at different time intervals for the reaction with aldehyde **2**.

As expected, the ion yields of *m/z* 305 significantly increased with reaction time in aldehyde **2**, and the same is true in the case of the ion at *m/z* 199. The intermediate ion at *m/z* 395, which is expected to be crucial, is found to be low abundant in both the aldehydes, because of which the changes in their ion yields are not prominent.

Thus, we moved to collision induced dissociation (CID) experiments on the ions at *m/z* 395 obtained from both the reactions to understand their stability. The spectra were recorded at different collision energy values (5-15 eV). The CID spectra of the ions *m/z* 395 from both the reactions showed exclusively one product ion at *m/z* 113 (Figure 7). The percentage of total ion current (%TIC) of *m/z* 395 was calculated from the ion abundances of *m/z* 113 and 395, and this value is plotted against collision energy (Figure 8). Figure 8 clearly reveals that the intermediate ion from aldehyde **2** is relatively more stable than that from aldehyde **1**. However, there are more than one transition states (**TS**) that are expected to appear at the *m/z* 395; hence, it is difficult to pinpoint which transition state is crucial for the differential reactivity of aldehydes **1** and **2**. Hence we moved to theoretical studies for better understanding on the BH reaction mechanism.

Computational studies

To gain insights into the observed differences in the rates of formation of isomeric MBH adducts quantum chemical calculations have been performed considering different mechanisms using both gas as well as solvent phases based on

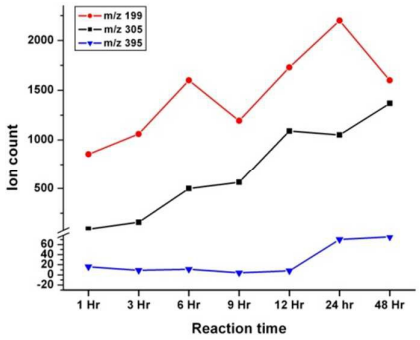


Figure 6. Ion counts at different time intervals for the reaction with aldehyde **1**.

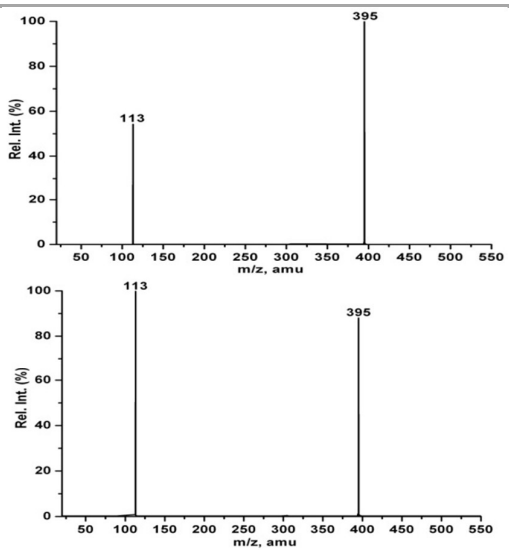


Figure 7. CID mass spectra of *m/z* 395 from aldehyde **2** (top) and aldehyde **1** (bottom) recorded at the collision energy of 5 eV.

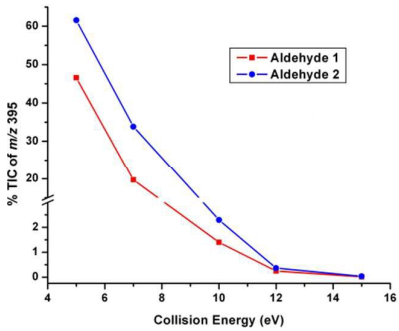
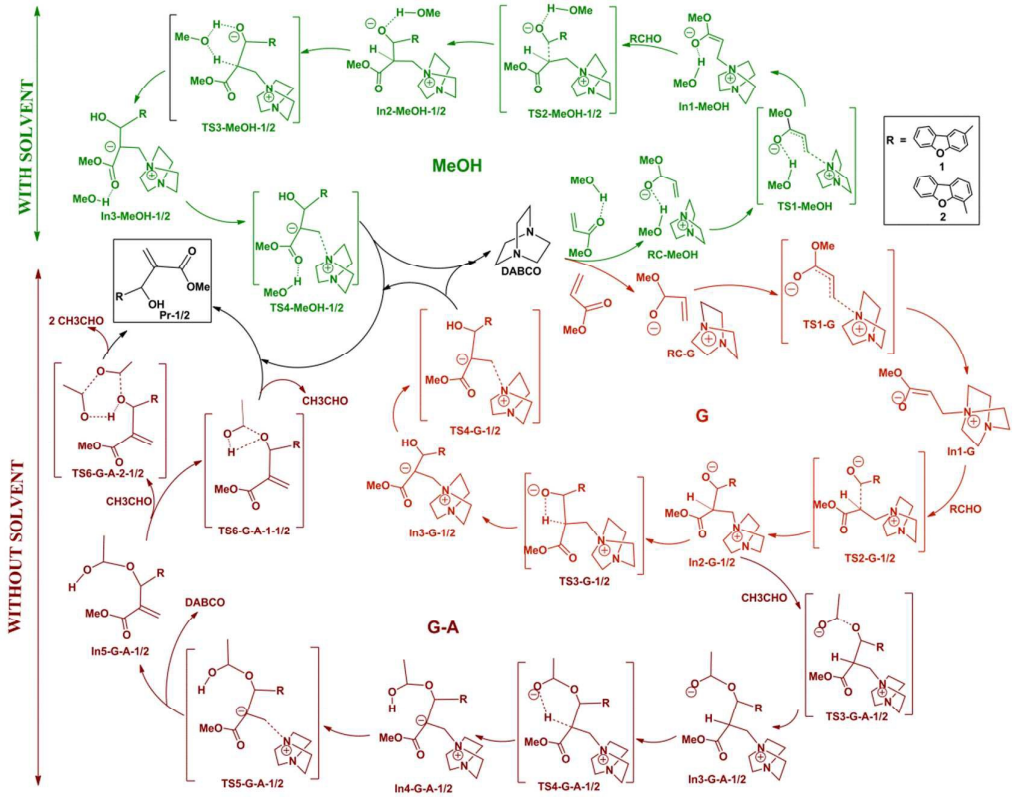


Figure 8. Plot of Percentage of total ion current (%TIC) values vs collision energy from the MS/MS spectra of the intermediates *m/z* 395 from aldehyde **1** and aldehyde **2**.



Scheme 5: Gas and solvent (methanol) phase reaction paths considered for the computational study.

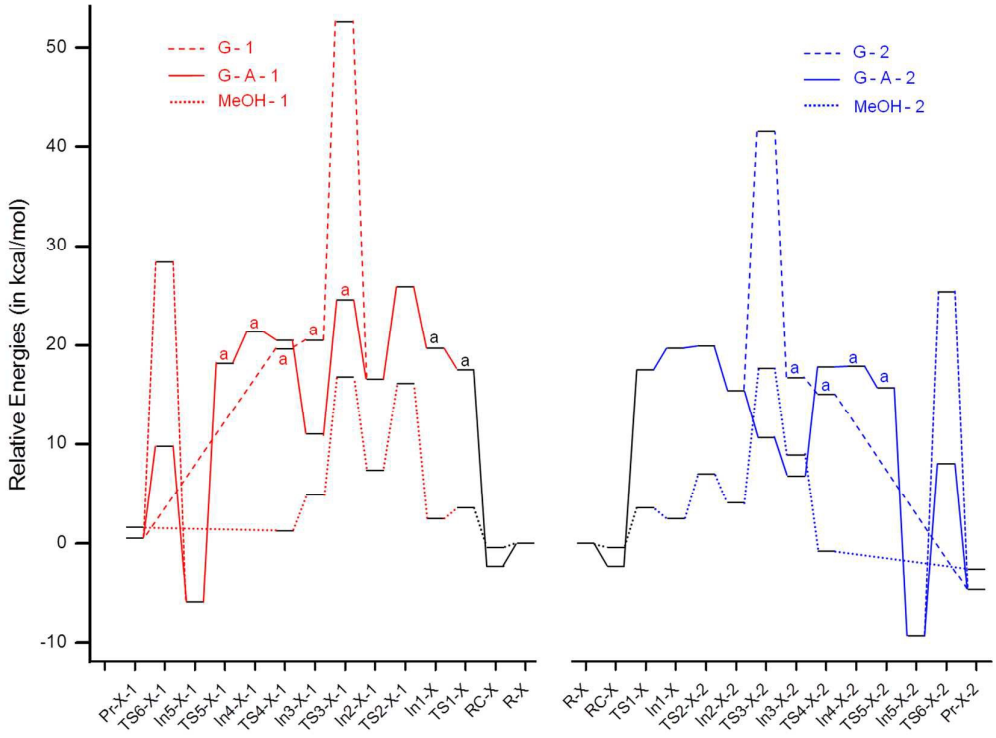


Figure 9. Gas and solvent phase reaction energy profiles for the considered MBH reaction obtained using the aldehydes **1** (red) and **2** (blue) at mPW1K/6-31+G(d,p) level of theory. a: represents the structures obtained at mPW1K/6-31+g(d,p)//HF/6-31+G(d,p) level of theory.

the previously reported pathways[16] (Scheme 5). The nomenclature (**-X-**) is given as '**-MeOH-**' for the structures obtained using methanol (as both explicit and implicit solvent), '**-G-**' for the structures obtained using gas phase and '**-G-A-**' for those obtained using gas phase and a second aldehyde molecule, which is reported to play a crucial role in the proton transfer step.[16a,16b] The structure bearing the aldehydes **1** and **2** are named with a suffix '**-1**' and '**-2**' respectively. IRC calculations have been performed to validate the transition states. The reaction profiles generated are depicted in Figure 9.

The gas and solvent phase reaction profiles were initially generated considering the paths '**G**' and '**MeOH**' as depicted in Scheme 5. After the formation of **In1-X** from methyl acrylate (**MA**) and **DABCO**, the aldehyde **1**/**2** attacks **In1-X**, proceeding through a C-C bond formation step, and forms **In2-X-1**/**In2-X-2** (-3.1/-4.2 and 4.9/1.6 kcal mol^{-1} considering **G** and **MeOH** respectively) via transition state **TS2-X-1**/**TS2-X-2** (6.2/0.3 and 13.7/4.5 kcal mol^{-1} for **G** and **MeOH** respectively). **In2-X-1**/**In2-X-2** then undergoes proton migration and forms **In3-X-1**/**In3-X-2**(3.9/1.3 and -2.5/4.8 kcal mol^{-1} for **G** and **MeOH** respectively) via transition state **TS3-X-1**/**TS3-X-2** (36.0/26.2 and 9.4/13.6 kcal mol^{-1} for **G** and **MeOH** respectively). These results clearly show that the proton migration step is the rate determining step (RDS) in both gas as well as solvent phases. However the activation energy for the C-C bond formation TS considering aldehyde **1** in solvent phase is ~4 kcal mol^{-1} higher in energy compared to the proton migration TS suggesting that both TSs play a key role during the reaction process in this case. The higher energy for the proton migration TS in gas phase compared to solvent phase might be due to the four membered transition state in the former case. **In3-X-1**/**In3-X-2** after **DABCO** elimination forms the final MBH adduct**.** The thermodynamic and kinetic energies, in general, along the reaction profile are observed to be much lower for **2** compared to **1** suggesting that the reaction with **2** should be faster than **1**. These are in accordance with the experimental results where **2** reacts faster in turn yielding the final MBH adduct compared to **1**. Though computational results suggest a huge effect of solvent on the considered MBH reaction, however experimental results suggest no effect of solvent on the reaction. Hence we proceeded further to look at an alternative mechanism[16a, 16b] considering a second equivalent of aldehyde. Previous reports by McQuade and coworkers,[16a] and Harvey and coworkers[16b] suggest the role played by the second equivalent of aldehyde in the proton transfer step. Keeping in mind the bulkiness of the aldehyde the aromatic moiety (R) is replaced with a methyl group which will reduce the computational cost.

The initial step before the proton transfer step is the addition of second aldehyde (**A**) to **In2-G** resulting in **In3-G-A-1**/**In3-G-A-2** (-5.6/-8.6 kcal mol^{-1}) via transition state **TS3-G-A-1**/**TS3-G-A-2** (8.0/-4.7 kcal mol^{-1}). **In3-G-A-1**/**In3-G-A-2** then undergoes proton migration and forms **In4-G-A-1**/**In4-G-A-2** (10.4/11.1 kcal mol^{-1}) via a 6-membered transition state **TS4-G-A-1**/**TS4-G-A-2** (9.5/11.0 kcal mol^{-1}). Similar to the results reported by Harvey and coworkers[16b] in the absence of protic species the activation energy for the 4-membered proton transfer transition state, **TS3-G-1**/**TS3-G-2** is much higher in energy compared to the 6-membered transition state **TS4-G-A-1**/**TS4-G-A-2**. **In4-G-A-1**/**In4-G-A-2** undergoes **DABCO** elimination with a subsequent proton transfer and aldehyde elimination, and forms the final MBH adduct. The transition state involving the elimination of second aldehyde and the simultaneous proton transfer for **TS6-G-A-1-1**/**TS6-G-A-1-2** is 34.4/34.7 kcal mol^{-1} which is much higher (~18.0 kcal mol^{-1}) in energy than **TS4-G-A-1**/**TS4-G-A-2**. As this step cannot be the RDS since the previous kinetic studies[16a] report the proton transfer step to be RDS therefore an alternative TS involving two molecules of aldehyde thereby resulting in a 6-membered TS is looked at. The TS involving an additional molecule of aldehyde lowers the energy drastically by ~15 kcal mol^{-1}, for **TS6-G-A-2-1** and **TS6-G-A-2-2** with an activation energy barrier of 15.7 and 17.3 kcal mol^{-1} respectively. The gas phase results are thus in accordance with the McQuade's proposal of MBH mechanism where in the absence of protic solvent the second equivalent of aldehyde plays a key role in proton transfer step. The virtually similar energy gaps considering **G-A** and **MeOH** paths might be the reason for the similar yields observed experimentally both in the presence and absence of protic solvent.

Similar to the **G** and **MeOH** energetics the thermodynamic and kinetic energies, along the reaction profile for **G-A** are observed to be much lower for **2** compared to **1** suggesting that the reaction with **2** should be faster than **1**. To understand the reason for the lower energies of **In2-X-2** and **TS2-X-2** compared to **In2-X-1** and **TS2-X-1** respectively, bond critical points for **TS2-X-1**, **In2-X-1**, **TS2-X-2** and **In2-X-2** are looked at for both gas as well as solvent phases. The electron density and its Laplacian values at the bond critical points (BCPs) are depicted in Figure 10 (gas phase) and Figure SX (solvent phase). The lower energies of aldehyde **2** considering both gas as well as solvent phases might be due to the interactions of the endocyclic oxygen (O_{EC}) which are observed in case of **2** while the aldehyde **1** is devoid of such interactions. This in turn might play a role in fastening the reaction process for **2**.

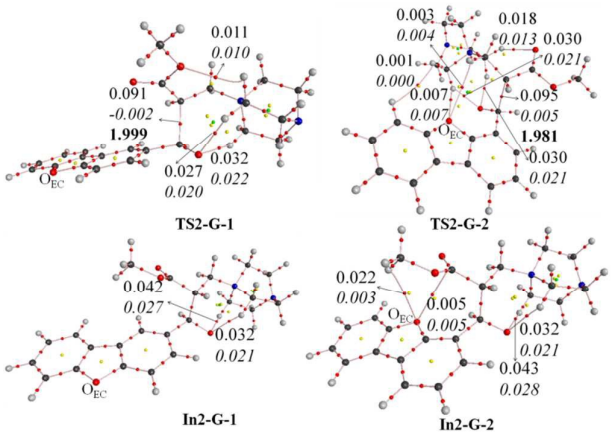


Figure 10. Bond critical points for **TS2-G-1**, **TS2-G-2, In2-G-1** and **In2-G-2**. Electron density values: normal, Laplacian of electron density: italics, Bond lengths: bold

Conclusions

In summary, we herein report Morita-Baylis-Hillman reaction of two isomeric dibenzofuran carbaldehydes (**1** and **2**) with different electrophiles in presence of DABCO as base catalyst. HPLC analysis of the reaction mixtures revealed that aldehyde **2** reacted at faster rate compared to its isomeric aldehyde **1** to give respective MBH adducts. *In situ* ESI-MS and MS/MS experiments concluded that the change in the rate of reaction was due to the stability of an intermediate (ion at *m/z* 395) formed during the course of MBH reaction. The gas and solvent phase reaction profiles gave insights for the observed differences in rates of formation of isomeric MBH adducts suggesting aldehyde **2** to be more reactive compared to **1**. The proton migration step is found to be the rate determining. In the absence of protic species an additional aldehyde molecule plays a key role in the proton migration which is in accordance with the McQuade's proposal of MBH mechanism.

Experimental Section

General Remarks

Melting points were measured with a Fischer-Johns melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets and absorptions are reported in cm^{-1}. NMR spectra were recorded on 300 (Bruker) and 500 MHz (Varian) spectrometers in appropriate solvents using TMS as internal standard and the chemical shifts are shown in δ scales. ^{13}C NMR spectra were recorded on 75 MHz spectrometers. High-resolution mass spectra were obtained by using ESI-QTOF mass spectrometry. All the experiments were monitored by analytical thin layer chromatography (TLC) performed on silica gel GF254 pre-coated plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Silica gel finer than 200 mesh was used for column chromatography. Yields refer to chromatographically and spectroscopically homogeneous materials unless otherwise stated. Appropriate names for all the new compounds were given with the help of ChemBioOffice 12.0; 2010. The solvents for column elution were purchased commercially and for mass spectral studies the solvents were purchased from Sigma Aldrich. Aldehydes **1** and **2** were synthesized by following the reported protocols.[13,14]

Mass spectrometry experiments: All the mass spectrometry experiments were performed using a quadrupole time-of-flight mass spectrometer (QSTAR XL, Applied Biosystems/MDS Sciex, Foster City, CA, USA) equipped with ESI ion source. The data acquisition was under the control of Analyst QS software (Applied Biosystems). All the samples were introduced into the source by flow injection (10 µL loop) using methanol as the mobile phase at a flow rate of 30 µL/min. The typical source conditions were: capillary voltage, 5 kV; declustering potentials DP1, 60 V; DP2, 10 V; focusing potential, 250 V; mass resolution 10000 (FWHM). Nitrogen was used as the curtain gas and the collision gas. For the CID experiments, the precursor ion of interest was selected using the quadrupole analyser and the product ions were analysed using the TOF analyser. The collision energies used were between 5 to 15 eV.

Procedure for computational studies: Calculations are performed on all the systems at mPW1K/6-31+G(d,p) level of theory as this method is proved to be better in locating the zwitterionic structures on the potential energy surface.[17] The TSs and Ins that could not be optimized at the aforementioned level are obtained at mPW1K/6-31+g(d,p)//HF/6-31+G(d,p) level of theory. Solvent phase calculations are performed using PCM. All the calculations are performed using Gaussian 09 programme package.[18] The BCPs are generated using AIM2000 software.[19]

General procedure for the preparation of MBH adducts 1A-D and 2A-D: A solution of aldehyde **1** or **2** (5 mmol), DABCO (5 mmol) and corresponding activated olefin (40 mmol) was stirred at RT for required time (Scheme 2). After that, the reaction mixture was diluted with ethyl acetate (20 mL), washed successively with 2N HCl (2 x 5 mL), water (2 x 5 mL) and saturated $NaHCO_3$ solution (5 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the crude residue thus obtained was chromatographed using EtOAc and hexane (10:90) over silica gel to give the corresponding MBH adducts **1A-D** and **2A-D** in very good yields.

Methyl 2-(dibenzo[b,d]furan-2-yl(hydroxy)methyl)acrylate (1A): Yield 75%: Light yellow syrup. ^1H NMR (300 MHz, $CDCl_3$) δ 7.94-7.82 (m, 2H), 7.58-7.44 (m, 2H), 7.43-7.35(m, 2H), 7.28 (t, J = 7.5Hz, 1H), 6.31 (s, 1H), 5.86-5.82 (m, 1H), 5.65 (s, 1H), 3.70 (s, 3H), 3.10 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 156.5, 142.1, 140.9, 135.8, 127.2, 126.0, 125.8, 122 .7, 121.2, 120.7, 118.8, 111.6, 111.4, 109.2, 73.1, 51.9. IR (neat) 3450, 2951, 1718, 1629, 1478, 1446, 1196, 1149, 1040, 816, 750cm^{-1}. MS (ESI) *m/z* 305 $[M+Na]^+$; HRMS (ESI) Calcd. for $C_{17}H_{14}O_4Na$: 305.0789, found: 305.0786.

Ethyl 2-(dibenzo[b,d]furan-2-yl(hydroxy)methyl)acrylate (1B): Yield 70%; White solid; m.p. 76-78 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99-7.84 (m, 2H), 7.61-7.49 (m, 2H), 7.47-7.37 (m, 2H), 7.35-7.27 (m, 1H), 6.35 (s, 1H), 5.85 (s, 1H), 5.73-5.67 (br s, 1H), 4.17 (q, J = 7.5 & 6.7 Hz, 2H), 3.15 (br, 1H), 1.25 (t, J = 7.5 & 6.7Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 156.3, 155.4, 142.5, 136.0, 126.9, 125.8, 125.0, 123.8, 122.4, 121.3, 120.4, 118.8, 111.4, 111.1, 72.5, 60.6, 13.8. IR (KBr) 3444, 2983, 1714, 1633, 1449, 1198, 1022, 960 cm^{-1}. MS (EI) *m/z* 296 $[M]^{+\cdot}$; HRMS (EI) Calcd. for $C_{18}H_{16}O_4$: 296.10486, found: 296.10536.

2-(Dibenzo[b,d]furan-2-yl(hydroxy)methyl)acrylonitrile (1C): Yield 93%;White Solid; m.p. 84-86 °C;^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 10.5 Hz, 2H), 7.56-7.50 (m, 2H), 7.48 -7.38 (m, 2H), 7.31 (t, J = 7.5 Hz, 1H), 6.11 (s, 1H), 6.01 (s, 1H), 5.39 (s, 1H), 2.80 (br s, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 156.0, 133.7, 129.8, 127.4, 126.2, 125.5, 124.5, 123.6, 122.8, 120.7, 118.8, 116.9, 111.9, 111.6, 74.0. IR (KBr) 3469, 2234, 1902, 1601, 1476, 1446, 1432, 1246, 1201, 1055, 952, 815, 744 cm^{-1}. MS (EI) *m/z* 249 $[M]^{+\cdot}$; HRMS (EI) Calcd. for $C_{16}H_{11}NO_2$: 248.07898, found: 248.07890.

2-(Dibenzo[b,d]furan-2-yl(hydroxy)methyl)cyclohex-2-enone (1D): Yield 63%;Syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02-7.87 (m, 2H), 7.65-7.28 (m, 5H), 6.71 (s, 1H), 5.72 (s, 1H), 2.52-2.37 (m, 4H), 2.10-1.99 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 156.3, 155.3, 147.3, 136.2, 127.0, 125.6, 122.5, 121.1, 120.6, 118.6, 115.9, 111.4, 109.5, 71.8, 38.3, 25.5, 22.3. IR (neat) 3411, 2924, 2853, 1666, 1510, 1478, 1444, 1374, 1244, 1196, 1020, 841, 750 cm^{-1}. MS (EI) *m/z* 292 $[M]^{+\cdot}$; HRMS (EI) Calcd. for $C_{19}H_{16}O_3$:292.10994, found: 292.10980.

Methyl 2-(dibenzo[b,d]furan-4-yl(hydroxy)methyl)acrylate (2A): Yield 99%; White solid; m.p. 95-97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 7.5 Hz, 1H), 7.84 (dd, J = 1.5 & 7.5 Hz, 1H), 7.52 (t, J = 8.3 Hz, 2H), 7.41 (td, J = 1.5 & 6.7 Hz, 1H), 7.36-7.25 (m, 2H), 6.32 (s, 1H), 6.17-6.12 (m, 1H), 5.80 (s, 1H), 3.75 (s, 3H), 3.44 (d, J = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 155.8, 153.1, 140.7, 136.8, 126.1, 125.2, 124.9, 123.9, 123.9, 122.6, 122.5, 120.4, 119.8, 111.5, 67.6, 51.6. IR (KBr) 3440, 3059, 2952, 1717, 1633, 1589, 1451, 1268, 1150, 1107, 1036, 960, 846, 756 cm^{-1}. MS (ESI) *m/z* 305 $[M+Na]^+$; HRMS (ESI) Calcd for $C_{17}H_{14}O_4Na$: 305.0789, found: 305.0783.

Ethyl 2-(dibenzo[b,d]furan-4-yl(hydroxy)methyl)acrylate (2B): Yield 97%; Light red colour syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 7.7 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.55-7.47 (m, 2H), 7.40 (t, J = 6.7 Hz, 1H), 7.33-7.26 (m, 2H), 6.31 (s, 1H), 6.14 (s, 1H), 5.79 (s, 1H), 4.17 (q, J = 6.7 Hz, 2H), 3.48 (br, 1H), 1.22 (t, J = 6.7Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 155.8, 153.1, 140.9, 126.9, 126.0, 125.2, 124.9, 124.0, 123.9, 122.6, 122.6, 122.5, 120.4, 119.9, 111.5, 67.8, 60.7, 13.7. IR (neat) 3504, 3062, 2989, 2912, 1706, 1628, 1423, 1283, 1184, 1035, 960, 834, 749 cm^{-1}. MS (EI) *m/z* 296 $[M]^{+\cdot}$; HRMS (EI) Calcd. for $C_{18}H_{16}O_4$: 296.10486, found: 296.10519.

2-(Dibenzo[b,d]furan-4-yl(hydroxy)methyl)acrylonitrile (2C): Yield 97%; Colourless Syrup. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.85 (m, 2H), 7.56-7.49 (m, 2H), 7.43 (td, J = 7.3 & 1.3 Hz, 1H), 7.39-7.28 (m, 2H), 6.14 (d, J = 1.1 Hz, 1H), 6.03 (d, J = 0.9 Hz, 1H), 5.88 (s, 1H), 3.12 (br s, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 152.9, 130.6, 127.4, 125.0, 124.5, 123.7, 123.2, 123.0, 121.0, 120.7, 116.8, 111.6, 69.3. IR (neat) 3434, 2925, 2228, 1716, 1584, 1451, 1425, 1265, 1150, 1044, 951, 837, 754 cm^{-1}. MS (EI) *m/z* 249 $[M]^{+\cdot}$; HRMS (EI) Calcd. for $C_{16}H_{11}NO_2$: 248.07898, found: 248.07890.

2-(Dibenzo[b,d]furan-4-yl(hydroxy)methyl)cyclohex-2-none (2D): Yield 80%; Black solid; m.p. 66-68 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.61-7.48 (m, 2H), 7.46-7.26 (m, 3H), 6.65 (t, J = 4.5 Hz, 1H), 6.12 (s, 1H), 3.83 (br s, 1H), 2.53-2.43 (m, 2H), 2.35 (q, J = 5.2 Hz, 2H), 2.08-1.98 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 155.8, 152.8, 147.1, 139.6, 126.8, 125.5, 125.0, 124.0, 123.8, 122.6, 122.5, 120.4, 119.5, 111.5, 67.3, 38.2, 25.5, 22.3. IR (KBr) 3418, 3059, 2926, 1667, 1588, 1474, 1423, 1378, 1250, 1186, 1024, 845, 755 cm^{-1}. MS (EI) *m/z* 292 $[M]^{+\cdot}$; HRMS (EI) Calcd. for $C_{19}H_{16}O_3$:292.10994, found: 292.10980.

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