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Unexpected Pd/C-catalyzed room temperature and atmospheric pressure hydrogenation of 2-methylenecyclobutanones

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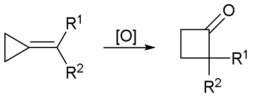
ABSTRACT

Pd/C-catalyzed hydrogenation reaction of 2-methylenecyclobutanones (2-MCBones) occurs at their exocyclic C=C sites regio-specifically to produce 2-substituted cyclobutanones, which are useful building blocks for the synthesis of drug and pesticide intermediates and are key intermediates in the total synthesis of many natural products. Surprisingly, atmospheric pressure H_2 in balloon can be used as the cheap, clean and safe reductant and the reaction occurs smoothly at room temperature (25 °C). Quantitative calculation demonstrates that the release of the intramolecular ring strain caused by the combined effect of the four-membered ring and exocyclic C=C bond in 2-MCBones provides additional dynamic driving forces for the reaction. The higher hydrogenation energy releasing of the exocyclic C=C than C=O was also found to be the causation for good regio-selectivity of the reaction. These new findings may broaden the understandings on the catalytic hydrogenation reactions of strained organic molecules.

1. Introduction

2-Substituted cyclobutanones are useful building blocks in synthetic organic chemistry that have been comprehensively employed for the synthesis of a series of drug and pesticide intermediates such as lactones, cyclopentanones, benzodiquinanes, naphthalenes, 9,10-dihydrobenzocyclooctene-7(8*H*)-ones, *etc* [1–4]. They are also key intermediates in the total synthesis of many natural products such as *α-Bisabolol, (-)-Debromofiliformin, (-)-Filiformin, (±)-Scirpene, (±)-a-Cuparenone, (±)-Herbertene, etc* [5–9]. Generally, 2-substituted cyclobutanones are synthesized *via* the ring-expansion reactions of cyclopropyl-contained compounds [5–17]. Among reported works, the oxidative ring expansion of methylenecyclopropanes (MCPs, Scheme 1, Eq. (1)) may be one of the most practical methods because of the concise preparation procedures of the starting materials from commercially available reagents [13–24]. The reactions once employed large amount of chemical oxidants such as *m*-chlorobenzoperoxoic acid (MCPBA), diisopropyl azodicarboxylate (DIAD), diethyl azodicarboxylate (DEAD) or cerium (IV) ammonium nitrate (CAN), which might generate solid wastes in large-scale production (Eq. (1)) [13–16]. Recently, during our continuous investigations on organoselenium catalysis [25–30], we developed a novel method for the synthesis of 2-substituted cyclobutanones *via* the organoselenium-catalyzed oxidative ring expansion reaction of MCPs [17]. The method employed H_2O_2 as the clean oxidant, but its substrate scope was limited to disubstituted MCPs to produce 2,2′-bis-substituted cyclobutanones, while the reactions with mono-substituted MCPs only led to a mixture of decomposed by-products. Moreover, because MCPs were prepared *via* the Wittig-reactions of cyclopropylidene ylid with carbonyls [18–20], the protocol inevitably generated the high molecular weight by-product triphenylphosphine oxide ($Ph_3P(O)$) that might lead to a lot of solid wastes in practical applications. Therefore, developing more atom-economic procedures for 2-substituted cyclobutanone synthesis is still crucial in the field.



[O] = MCPBA, DIAD, DEAD or CAN (1)

On the other hand, since cyclobutanone is a commercially available chemical that can be purchased at an acceptable price [31], it may serve as a good building block in organic synthesis for introducing four-membered carbocycles into the molecules. In 2014, we reported that, by using a simple condensation of cyclobutanone with aldehydes, once

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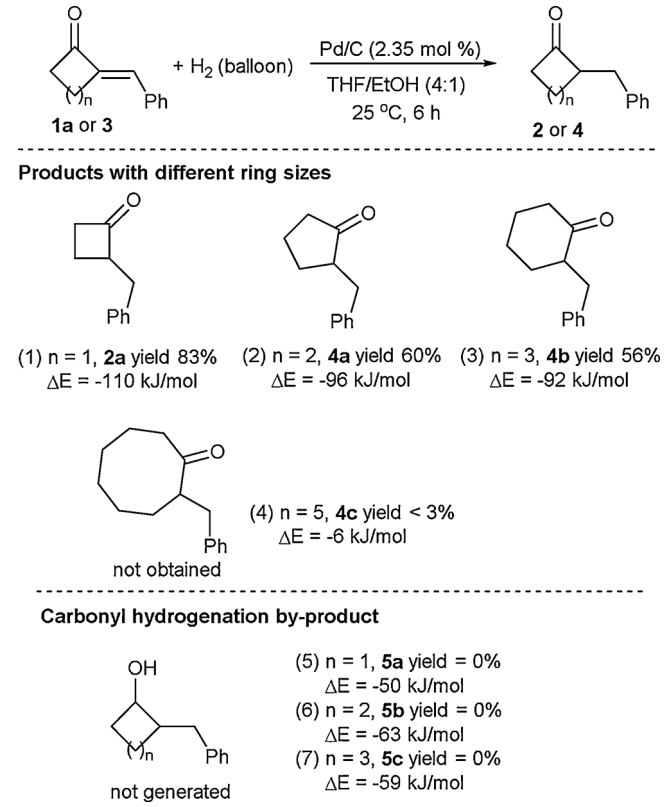
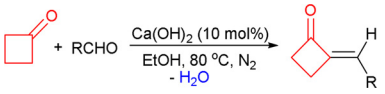


Scheme 1. Synthesis of 2-substituted cyclic ketones **2a** and **4a-c** and calculation of the reaction energy.

hardly obtained 2-methylenecyclobutanones (2-MCBones) could be directly synthesized (Scheme 1, Eq. (2)) [32]. In the reaction, cheap, low-loading (10 mol%) and removable $Ca(OH)_2$ was employed as catalyst and no waste was generated other than the water [33–35]. Recently, we were surprised to find that the molecules were so reactive that their catalytic hydrogenation reaction could be performed at atmospheric pressure and under room temperature. Different from the hydrogen transfer reactions [36–38], the reaction employed H_2 (just in a balloon) as an efficient reductant. It did not require expensive metal complexes [39], while the simple, commercial available and recyclable Pd/C was the preferable catalyst. In regardless of the multiple reaction sites in 2-MCBones as well as the possible cyclobutyl ring opening side-reactions, the reaction occurred at the exocyclic C=C bond regio-specifically. Herein, we wish to report our findings.



(2)

2. Experimental

2.1. General methods

Solvents were of analytical purity (AR) and were purchased from reagent merchant. 2-MCBones were synthesized *via* the literature method [40]. NMR spectra were recorded on Bruker Avance instruments (600 or 400 MHz for ^1H NMR and 150 or 100 MHz for ^{13}C NMR) using $CDCl_3$ as solvent and Me_4Si as internal standard. Chemical shifts for ^1H NMR were relative to internal Me_4Si (0 ppm) and *J*-values were shown in Hz. Theoretical calculations were conducted by GaussView 5 software (Gaussian09 package) using semi-empirical molecular orbital method (PM6). Elemental analysis was performed on an Elementar Vario EL cube instrument.

2.2. General procedure for the hydrogenation reaction of 2-MCBones

25 mg of Pd/C (containing 0.0235 mmol of Pd) and a magnetic bar were added into a reaction tube charged with N_2. A solution of 1.0 mmol of 2-MCBone **1** (synthesized *via* the method in ref. [40] in 10 ml of anhydrous THF/EtOH (volume ratio = 4:1) was injected into the reaction tube, which was then equipped with a balloon charged with H_2. The mixture was magnetically stirred at room temperature (25 °C) for 6 h. The solvent was evaporated under vacuum and the residue was separated by flash column chromatogram (eluent: petroleum ether-EtOAc 20:1) to give the 2-substituted cyclobutanones **2** in related yields (*vide infra*).

2.3. Method for the determination and calculation of C-mass balance

C-mass balance was calculated by the following equation:

C-mass balance = (carbon weight in the product + carbon weight in the by-products)/carbon weight in the reactant

Carbon weight in the by-products was determined by elemental analysis. For example, in the reaction of **1a** (Table 3, entry 1), after getting the desired product **2a** by flash column chromatogram, acetone-methanol 1:1 was used as high-polar solvent to wash out the rest by-products on silica gel chromatographic column. Solvent of the combined solution of the by-products was removed under vacuum and the residue was weight and sent to elemental analysis to determine the carbon content. For the reaction of **1a** (Table 3, entry 1), 133.0 mg of product **2a** (containing 82.46% of C) and 30.4 mg of by-products was obtained. Elemental analysis indicated the by-products contained 72.51% of C. Therefore, the C-mass balance could be calculated as:

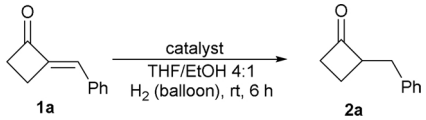
C-mass balance = (133.0 mg × 82.46% + 30.4 mg × 72.51%)/[11 mmol (each molecular of **1a** contained 11 C) × 12.01 mg/mmol (atom weight of C)] = 99.7%

3. Results and discussion

3.1. Catalyst screenings

Catalyst screenings were initially performed and for a 1 mmol-scale reaction, 5 mg of catalyst was employed (Table 1). The 2-MCB reactant dissolved well in THF, while alcohols, such as EtOH, were good solvents

Table 1
Catalyst screenings[a].



Entry	Catalyst	**2a** yield (%)
1	Raney Ni	trace
2	10%Pt/C	trace
3	10%Ru/C	trace
4	10%Pd/C	21
5	Pd@PANI	11
6	Ru@PANI	0
7	Cu@PANI	0
8	Pd@Al	13
9	Pd&Cu@Al	15
10	Cu&Fe@Al	0
11	$PdCl_2$	5
12	$Pd(OAc)_2$	8
13	$Pd(PPh_3)_4$	7

[a] 1 mmol of **1a**, 5 mg of catalyst (or a 1 × 1 piece of catalyst for Pd@Al, Pd&Cu@Al and Cu&Fe@Al) and 10 ml of THF/EtOH (4:1) were employed.

for catalytic hydrogenation reaction [37]. Therefore, THF/EtOH (4:1) was employed as the reaction solvent. We first tested the Raney Ni-catalyzed hydrogenation of 2-MCBone **1a** with atmospheric pressure H_2 in a balloon under room temperature (rt = 25 °C), but almost no reaction occurred (Table 1, entry 1). Other commercially available regular catalysts, such as Pt/C, Ru/C and Pd/C (catalytic metal weight contents were all 10%) were then examined, and Pd/C was screened out to be the most active one, affording **2a** in 21% yield (Table 1, entries 4 *vs.* 1–3). Pd@PANI [40–44], Ru@PANI [45], Cu@PANI [46], Pd@Al [47], Pd&Cu@Al [48] and Cu&Fe@Al [49], which were novel catalysts developed by our group recently, were employed but failed to optimize the reaction any more (Table 1, entries 5–10). Homogeneous Pd catalysts, such as $PdCl_2$, $Pd(OAc)_2$ and $Pd(PPh_3)_4$ were tested, but resulted in poor **2a** yield and a series of unidentified by-products were observed in thin-layer chromatography (TLC). The above results demonstrated that only Pd catalysts worked for the reaction (Table 1, entries 4,5,8,9,11–13 *vs.* 1–3,6,7,10), and Pd/C was preferable not only for the higher product yield, but also for the good availability. Moreover, it was found that the product yield could be enhanced by increasing the Pd/C catalyst amount, and 25 mg of Pd/C for 1 mmol scale reaction was the inflection point of the curve, where **2a** was obtained in 81% yield (Fig. 1). Further increasing Pd/C amount could not improve the reaction (Fig. 1), which was probably because of the limitation of the contact of the two-phase reactants of **1a** with H_2.

3.2. Solvent screenings

Solvent screenings for the reaction were performed and the results were summarized in Table 2. The reaction did not occur in non-polar solvents such as toluene and cyclohexane, or chloro-contained solvents such as CH_2Cl_2 and $CHCl_3$ (Table 2, entries 1–4), while polar solvents such as THF, 1,4-dioxane, MeCN, DMSO or DMF also led to very poor **2a** yields (Table 2, entries 5–9). Alcohol solvents, such as MeOH and EtOH, were more preferable, affording **2a** in 29–30% yields (Table 2, entries 1011). Interestingly, stirring **1a** in EtOH could produce **2a** in 8% yield even without using H_2 balloon as the hydrogen source, showing that alcohol might participate the reaction as H-donor in the presence of Pd catalyst and the generated acetaldehyde might be reduced to EtOH again by H_2. This process could accelerate the hydrogen process because it occurred in a homogeneous solution, other than the hydrogenation with H_2 occurred between two-phase reactants [37]. Based on this finding, EtOH was added in THF (which could dissolve 2-MCBone well) to improve the reaction solvent and parallel experimental results demonstrated that THF/EtOH = 4:1 was the best volume ratio, giving **2a** in 81% yield (Fig. 2).

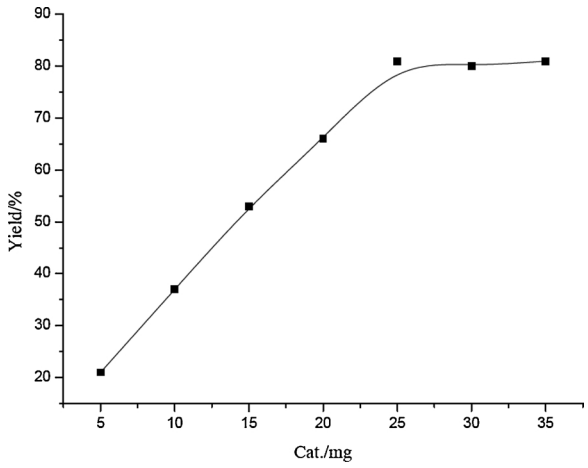
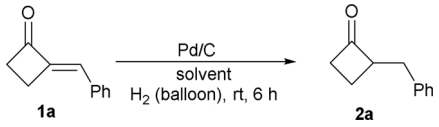


Fig. 1. Catalyst amount screenings [reaction conditions: 1 mmol of 2-MCBone, 10 ml of THF/EtOH (4:1), 25 °C, 6 h, H_2].

Table 2
Solvent screenings[a].

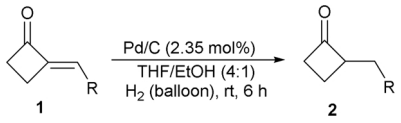


1a 2a

Entry	Solvent	**2a** yield (%)
1	toluene	trace
2	cyclohexane	trace
3	CH_2Cl_2	trace
4	$CHCl_3$	trace
5	THF	12
6	1,4-dioxane	trace
7	MeCN	7
8	DMSO	trace
9	DMF	trace
10	MeOH	29
11	EtOH	30

[a] 1 mmol of **1a**, 25 mg of Pd/C and 10 ml of solvent were employed.

Table 3
Substrate extensions[a].



1 2

Entry	R (**1**)	**2**: yield (%)[b]	C-mass balance (%)[c]
1	Ph (**1a**)	**2a**: 83	99.7
2	Ph (**1a**)	**2a**: 80[d], 81[d,e], 78[d,e], 76[d,e]	–
3	4-MeC_6H_4 (**1b**)	**2b**: 78	99.6
4	4-$Bu^tC_6H_4$ (**1c**)	**2c**: 56	99.5
5	4-$MeOC_6H_4$ (**1d**)	**2d**: 77	99.0
6	3-$MeOC_6H_4$ (**1e**)	**2e**: 86	99.2
7	2-$MeOC_6H_4$ (**1f**)	**2f**: 81	99.1
8	4-FC_6H_4 (**1 g**)	**2g**: 71	99.4
9	4-$CF_3C_6H_4$ (**1 h**)	**2h**: 69	99.3
10	1-$C_{10}H_7$ (**1i**)	**2i**: 75	99.5
11	2-C_4H_3S (2-thiophene, **1 j**)	**2 j**: 91	99.1
12	*c*-C_6H_{11} (**1k**)	**2k**: 46	99.5

[a] 1 mmol of **1a**, 25 mg of Pd/C and 10 ml of solvent were employed.
[b] Isolated yields based on **1**.
[c] Method of C-mass balance determination and calculation were given in experimental section 2.3.
[d] Reaction in 10 mmol scale.
[e] Reaction with recycled Pd/C catalyst.

3.3. Investigations on the effects of reaction temperature and time

Owing to the high reactivity of the 2-MCBone reactant, the hydrogenation reaction occurred at room temperature smoothly in high yield and turnover frequency. As shown in Fig. 3, the product yield of the hydrogenation reaction was almost constant in the range of 25–100 °C, but for energy saving consideration, room temperature reaction condition, as we initially used, should be preferable. The reaction afforded **2a** in 43% yield within 1 h. The yield gradually increased and reached its peak at 6 h, which should be the most favorable reaction time (Fig. 4). Moreover, after heating **2a** at 100 °C under the standard reaction conditions (1 mmol of **2a**, 25 mg of Pd/C, 10 ml of THF/EtOH, 6 h, H_2), more than 94% of the chemical could be recovered again by flash column chromatography separation, showing that the produced 2-substituted cyclobutanones was stable under the reaction conditions and it did not decompose at the temperature below 100 °C. Thus, the slight decrease in yields upon increasing the reaction temperature

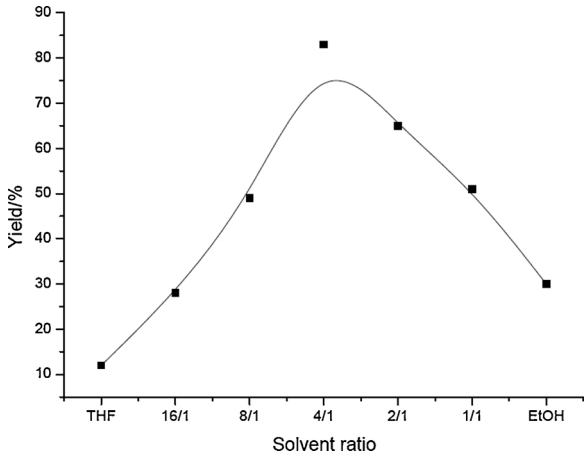


Fig. 2. THF/EtOH ratio screenings (reaction conditions: 1 mmol of 2-MCBone, 25 mg of Pd/C, 10 ml of THF/EtOH, 25 °C, 6 h, H_2).

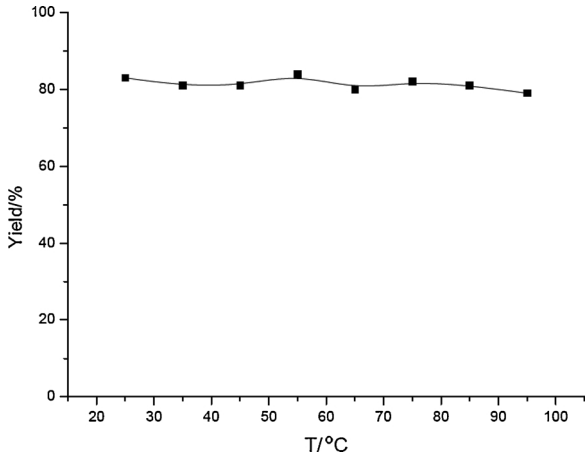


Fig. 3. Effects of the reaction temperature (reaction conditions: 1 mmol of 2-MCBone, 25 mg of Pd/C, 10 ml of THF/EtOH, 6 h, H_2).

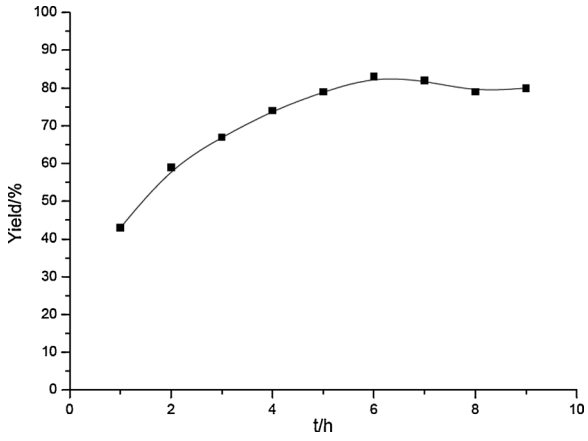


Fig. 4. Effects of the reaction time (reaction conditions: 1 mmol of 2-MCBone, 25 mg of Pd/C, 10 ml of THF/EtOH, 25 °C, H_2).

(Fig. 3) may be rather attributed to catalyst deactivation or to the occurrence of other side-effects other than the product decomposition. This is supported by the fact that reactions do not come to completion even for very long reaction times (Fig. 4).

3.4. Substrate extensions

A series of 2-substituted cyclobutones were then synthesized *via* this hydrogenation reaction under the optimized reaction conditions (Table 3). The product yield did not decrease in a 10 times scale-up reaction (Table 3, entries 2 *vs.* 1), and 1.28 g (in 80% yield) of 2-benzylcyclobutan-1-one (**2a**) was synthesized smoothly. The catalyst could be recovered by centrifugal separation and was reusable for at least three times without deactivation (Table 3, entry 2). Both electron-enriched and -deficient 2-MCBones were favorable substrates for the reaction (Table 3, entries 3–9), and the electron-enriched substrates were generally more preferable than the electron-deficient ones (Table 3, entries 3, 5–7 *vs.* 8,9). Interestingly, 2-(2-methoxybenzyl)cyclobutan-1-one (**2f**) could be synthesized in even higher yield than that of **2d**, in regardless of the higher steric hindrance in substrate caused by the *ortho*-substituent on aryl (Table 3, entries 7 *vs.* 5). Similarly, (*E*)-2-(naphthalen-1-ylmethylene)cyclobutan-1-one (**1i**), as an example of substrate bearing bulky group, was also smoothly converted into the related product **2i** in good yield (Table 3, entry 10). It was notable that the reaction was tolerant to sulfur-contained group, which might cause the Pd catalyst poisoning in many reactions, and the reaction of substrate **1j** led to product **2j** in excellent yield (Table 3, entry 11). The reaction was also applicable for aliphatic substrate, such as **1k**, and produced the desired 2-substituted cyclobutanone **2k** in moderate yield (Table 3, entry 12). C-mass balance of the reaction was calculated and it was generally high (> 99%) in all of the examples (Table 3, entries 1,3–12).

3.5. Mechanism study

A series of methylene-substituted cyclic ketones **1a** and **3a-c** were employed in the hydrogenation reaction for comparison to judge the effect of substrate ring sizes on the reaction (Scheme 1). Using (*E*)-2-benzylidenecyclopentan-1-one (**3a**) or (*E*)-2-benzylidenecyclohexan-1-one (**3b**) as substrate resulted in decreased product yield (Scheme 1, runs 2,3 *vs.* 1). Bearing a very large eight-membered ring in substrate, the hydrogenation reaction of 2-benzylcyclooctan-1-one (**3c**) was difficult to occur and only traces of the desired product were observed on thin-layer chromatographic (TLC) plate (Scheme 1, run 4). To reveal the reasons for the above experimental results, quantitative calculations were performed with GaussView 5 software using semi-empirical molecular orbital method (PM6). It was found that the reaction of **1a** to **2a** released ca 110 kJ/mol of energy (Scheme 1, run 1). With the increasing of the substrate ring sizes, the released energies of the reactions of **3a** to **4a** and **3b** to **4b** decreased to 96 and 92 kJ/mol respectively (Scheme 1, runs 2–3). In the reaction of the eight-membered ring-contained substrate **3c** to **4c**, only 6 kJ/mol of energy was released (Scheme 1, run 4). The reduced reaction energy releasing might be the reason of the decreased product yields, in good accordance with the results of parallel experiments. Therefore, it was demonstrated that the hydrogenation reaction of the C=C bond of 2-MCBones could partially release the high intramolecular ring strain caused by the combined effect of the small ring and exocyclic C=C bond of the substrate and provide additional driving forces to facilitate the reaction processes under mild conditions. Chemo-selective hydrogenation reactions of C=C *versus* C=O bonds over noble metals may attribute to the grater affinity of the metals for C=C [50–52]. Moreover, the quantitative calculation results have also indicated that, the hydrogenations of carbonyls in **2a**, **4a** and **4b** to produce alcohols **5** released less energy than the related C=C bond hydrogenation (Scheme 1, runs 5 *vs.* 1, 6 *vs.* 2, 7 *vs.* 3), and these results could well explain the reason of the high regio-selectivities of the reactions.

4. Conclusions

In conclusion, an unexpected Pd/C-catalyzed room temperature and

atmospheric pressure hydrogenation reaction of 2-methylenecyclobutanones was found to be an efficient method for the synthesis of 2-substituted cyclobutanones, which were useful synthetic intermediates for many drug and pesticide intermediates as well as the total synthesis of natural products. The method employed commercially available terminal starting materials such as cyclobutanone and aldehydes and could be performed under mild reaction conditions using atmospheric pressure H_2 in balloon as the cheap, clean and safe reductant. Quantitative calculations demonstrated that the release of the intramolecular ring strain caused by the combined effect of the four-membered ring and exocyclic C═C bond in the intermediate 2-MCBones provided additional dynamic driving forces for the reaction and the high regio-selectivity of the reaction was caused by the higher hydrogenation energy releasing of C═C than C═O. These new findings have broadened the understandings on the catalytic hydrogenation reactions of strained organic molecules.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110450.

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