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Catalyst-Free Photodecarbonylation of ortho-Amino Benzaldehyde

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It is almost a consensus that decarbonylation of aldehyde group (-CHO) need to not only be mediated by transition metal catalysts, but also react under severe reaction conditions (high temperature and long reaction time). In this work, inspired by the "conformational-selectivity-based" design strategy, we broke this consensus and discovered a catalyst-free photodecarbonylation of aldehyde group. It revealed that the decarbonylation can be easily achieved with visible light irradiation by introducing the tertiary amine into the orthoposition of aldehyde group. A diverse array of tertiary amines are tolerated by our photodecarbonylation under mild conditions. Furthermore, the (QM) computations of mechanism and the experiments on well-designed special substrates revealed that our photodecarbonylation depends on the conformational specificity of aldehyde group and tertiary amine, and performs through an unusual [1, 4]-H shift and a subsequent [1, 3]-H shift.

The decarbonylation of aldehyde group is one of the essential protocols in chemistry.¹ Besides its wide use in the synthesis of natural products for over half a century,² such as its applications to the region-selectivity in Diels-Alder reaction³ and domino oxa-Michael-aldol reaction,⁴ and its well-known benefit in the supply of in situ CO,⁵ it also has been recently convincingly shown the potential in the selective conversions of biorenewable materials for chemical feedstock and energy applications.⁶ Hence, development of effective and versatile decarbonylation method is of great methodological and chemosynthetic interest. In the past decades, various systems

of decarbonylation have been investigated successfully. Of those systems, to the best of our knowledge, the transition metal catalysts such as Ir,⁷ Rh,⁸ Ru,⁹ Pd¹⁰ and Ni¹¹ (Scheme 1a), and even the chemical scavenger for the evolved CO¹² were considered necessary. However, most of the existing metal catalysts are costly and not easily available, and the selected CO-scavenger are generally not environmentally friendly. Not only those, the reported decarbonylation reactions were often done under both high temperature (over 66 °C) and long reaction time (over 24 h, even to 96 h) with limited substrate scope.¹³ Therefore, it is highly desirable to overcome the above drawbacks, and develop an efficient catalytic process for the decarbonylation of aldehyde group under mild conditions (low temperature and short reaction time) and without metal catalysts and CO-scavenger.

a) Previous work

Transition Metal Mediated Decarbonylation



b) This work



Scheme 1. a) Previous transition metal catalyst mediated decarbonylation of aryl aldehydes. b) Proposed visible-light-promoted decarbonylation (photodecarbonylation) of 2-amino benzaldehyde under mild conditions without any catalysts. DMPU = 1, 3-Dimethyl-3, 4, 5, 6-tetrahydro-2(1H)-pyrimidinone.

In our previous work,¹⁴ we suggested an intramolecular photocyclization of carbonyl groups and tertiary amines whose photocyclization mechanism involved a [1, 6]-H shift and a subsequent radical-radical coupling (Figure 1a). As we know, ketone compounds are inclined toward homolysis to diradical properties under irradiation of visible light.¹⁵ We wonder whether a different consequence could be formed in aldehyde

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compounds. Herein. guided bv the characterized conformational specificity of above carbonyl groups and tertiary amines that the oxygen atoms of carbonyl groups should direct toward the tertiary amines, we have developed a "conformational-selectivity-based" design strategy (Figure 1b). In this design strategy, we hypothesized that once the carbonyl groups are changed to the specific aldehyde group by replacing the R group with a very small hydrogen atom, the aldehyde group and tertiary amines could present different conformations those correspond to different photochemical reactions. To be specific, due to the rotation of aldehyde group, the oxygen atom of aldehyde group on one hand can di t: toward the tertiary amines (O-State in Figure 1b), resulting above-mentioned intramolecular photocyclization which oc s through the [1, 6]-H shift and radical-radical coupling; on o hand can keep away from the tertiary amines and the hydro n atom of aldehyde group can direct toward the tertiary am s (H-State in Figure 1b), resulting a photodecarbonylation w h occurs through an unusual [1, 4]-H shift and a subsequent [1 H shift. Therefore, we believe that if the tertiary amines e introduced into the ortho-position of aldehyde group, e obtained 2-amino benzaldehyde compounds may present e H-State, and under visible light irradiation, they may could o ır the photodecarbonylation of aldehyde group under d conditions and without any catalysts (Scheme 1b).





Figure 1. "Conformational-selectivity-based" design strategy for the photodecarbonylation of 2-amino benzaldehyde.

Fortunately, our calculation¹⁶ found that when the morpholine ring was introduced into the *ortho*-position of aldehyde group, the obtained 2-morpholinobenzaldehyde (**1a**) would prefer H-State to O-State in both ground state and excited state due to the thermodynamic feasibility (Figure 1c). Thus, **1a** was chosen to initiate the reaction optimization (Table 1). We first screened a series of solvents under operationally simple (425 nm LED and argon atmosphere) and very mild (room temperature and 6 h reaction time) photochemical

Table 1. Reaction optimization^[a] for the photodecarbonylation of 1a.

| | | Ar r.t., 6 h | | coţ |
|-------|--------------------------------------|-----------------|--------------------------|-------------------------|
| | ں 1 <i>a</i> | | 2a | |
| Entry | Solvent | Additive | Yield [%] ^[b] | CO [ppm] ^[c] |
| 1 | CH₃CN | 425 nm LED | - | - |
| 2 | CH ₃ OH | 425 nm LED | - | - |
| 3 | DCM | 425 nm LED | - | - |
| 4 | CH ₂ ClCH ₂ Cl | 425 nm LED | trace | - |
| 5 | Dioxane | 425 nm LED | trace | - |
| 6 | EtOAc | 425 nm LED | trace | - |
| 7 | Toluene | 425 nm LED | trace | - |
| 8 | CH_3COCH_3 | 425 nm LED | trace | - |
| 9 | DMSO | 425 nm LED | 33% | > 1000 |
| 10 | DMA | 425 nm LED | 40% | > 1000 |
| 11 | DMF | 425 nm LED | 57% | > 1000 |
| 12 | THF | 425 nm LED | 58% | > 1000 |
| 13 | HMPA | 425 nm LED | 64% | > 1000 |
| 14 | NMP | 425 nm LED | 65% | > 1000 |
| 15 | DMPU | 425 nm LED | 75% | > 1000 |
| 16 | DMPU | avoided light | - | - |
| 17 | DMPU | 254 nm | - | - |
| 18 | DMPU | 365 nm | 21% | \sim 1000 |
| 19 | DMPU | 570 nm | - | - |
| 20 | DMPU | white light | 52% | > 1000 |
| 21 | DMPU | 425 nm LED, O2 | 33% | > 1000 |

[a] Reactions were conducted with **1a** (0.3 mmol), solvent (3 mL), room temperature, 6 h, under an argon atmosphere. [b] Isolated yield. [c] The concentration of the generated CO gas was detected by the "gas sampling pump".

With the optimized conditions in hand, we then explored the substrate scope by introducing various tertiary amines into the *ortho*-position of aldehyde group (Scheme 2). For naphthenic

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amines, besides above-mentioned morpholine (1a), the 2, 6dimethylmorpholine (1b), piperidine (1c), 2-methylpiperidine (1d) and azepane (1e), also exhibited good reactivity, furnishing the decarbonylation products (2b-2e) in 64, 63, 71 and 60% yields, respectively. The naphthenic amines containing aryl groups were also considered. Such as 4-phenylpiperazine (1f), it produced the decarbonylation product (2f) in a relatively low but acceptable yield (55%). For alkyl amines, the dimethylamine allyl(methyl)amine (1g), (1h) and (2methoxyethyl)(methyl)amine (1i) produced the decarbonylation products (2g-2i) only in 48, 46 and 44% yields, respectively. Obviously, the yields produced by alkyl amines actually barely satisfactory. However, the alkyl amines containing aryl groups, such as benzyl(methyl)amine (1j), (4methoxybenzyl)(methyl)amine (1k), 4-((methylamino)methyl) benzonitrile (11), benzyl(ethyl)amine (1m), benzyl(butyl)amine (1n) and dibenzylamine (1o), afforded the decarbonylation products (2j-2o) in 56, 50, 55, 58, 53 and 61% yields, respectively. Thus, the introduction of aryl groups to alkyl amines partly could improve the yields of decarbonylation products. In addition, two special tertiary amines were found. One was tetrahydroisoquinoline (1p) tolerated not only by our photodecarbonylation with 60% yield of decarbonylation product (2p), but also by the previously reported photocyclization with trace yields of dehydrated cyclization product (**3p**). The other one was pyrrolidine (**1q**) only tolerated by the photocyclization with 52% yield of dehydrated cyclization product (3q). Overall, despite special cases, most tertiary amines are tolerated by our photodecarbonylation.



Scheme 2. Substrate scope with respect to 2-amino benzaldebyde. The reaction time was prolonged to 12 h for Pearle 11. Solated View. The concentration of the generated CO gas was detected by the "gas sampling pump" (> 1000 ppm for 1a-1p).

We next turned our attention to the substituents in the benzene ring of 1a to further expand the substrate scope (Scheme 3). For electron-withdrawing groups, they significantly improved the yields of decarbonylation products, whether in ortho-, meta- or parapositions of tertiary amine. Such as fluorine in meta-position (1aa), chlorine in ortho- (1ab) and meta- (1ac and 1ad) positions, bromine in meta- (1ae) and para- (1af) positions, and formonitrile in meta-(1ag) and para- (1ah) positions, they afforded decarbonylation products (2aa-2ah) in high yields of 95, 91, 90, 76, 88, 79, 81 and 89%, respectively. However, there was an exception that chlorine in paraposition (1ai) furnished decarbonylation product (2ai) only in 65% yield. Although relatively low, it is also a good yield. For electrondonating groups, the methyl in meta- (1aj) and para- (1ak) positions, and methoxyl in *meta*-position (1al), provided decarbonylation products (2aj-2al) only in 53, 47 and 56% yields, respectively. The yields of decarbonylation products (2am-2an) would further decrease to trace amounts when methoxyl was in para-position (1am-1an). Thus, the electron-donating groups, contrary to the electron-withdrawing groups, were unfavorable to our photodecarbonylation. By the way, we replaced the benzene ring of 1a by pyridine ring (1ao), also producing decarbonylation product (2ao) in good yield (68%). It suggested that it is aryl aldehydes, not just benzaldehydes that could be tolerated bv our photodecarbonylation by introducing tertiary amine.



Scheme 3. Substrate scope with respect to 1a. Isolated yield. The concentration of the generated CO gas was detected by the "gas sampling pump" (> 1000 ppm for 1aa-1al and 1ao).

Considering the above experimental results of substrate scope, the first key question is whether the photodecarbonylation depends on the conformational specificity (H-State or O-State) of aldehyde group and tertiary amine hypothesized by our "conformationalselectivity-based" design strategy. The free energy profiles from O-State to H-State for all the substrates in Scheme 2 (**1a-1q**) in ground states were calculated (Figure 2a).¹⁶ We can see that the H-States of all calculated substrates but **1p** and **1q**, were more stable than their

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corresponding O-States. For example, the H-State of 1a was 3.29 kcal/mol more stable than its O-State. Thus, these substrates tended to H-State. In striking contrast, the 1q was inclined to O-State since its O-State was more stable (4.44 kcal/mol) than the H-State. As to 1p, it preferred to be shared nearly half-and-half by O-State and Hstate as its O-State and H-State shared an almost equivalent stability (0.00 vs -0.02 kcal/mol). Besides the ground states, the similar results were found in the computations of excited states (Figure 2b). Combined with the experimental results, we can see that the substrates tending to H-State or O-State, only occurred corresponding photodecarbonylation (1a-1o) or photocyclization (1q), while the substrates neutral to H-state and O-state, occurred both photodecarbonylation and photocyclization (1p). Thus, as hypothesized, different conformations (H-State or O-State) of tertiary amine and aldehyde group may determine different photoreactions (photodecarbonylation or photocyclization).



Figure 2. Conformational specificity of aldehyde group and tertiary amines (mechanistic studies-1). O-State, H-State, 1, A, C and 2 refer to Figure 1.



Figure 3. Reaction profiles based on the reaction mechanisms in Figure 1b (mechanistic studies-2). O-State, H-State, 1-3 and A-E refer to Figure 1.

The next key question is whether the photodecarbonylation occurs through an [1, 4]-H shift and a subsequent [1, 3]-H shift. Based on the reaction mechanisms proposed in Figure 1b, we calculated the reaction profiles¹⁶ for **1a**, **1p** and **1q** (Figure 3). We can see that under H-State, once the substrate (1 state) jumped into the excited state (A state), it could occur [1, 4]-H shift with low energy barrier (10.25, 10.96 and 9.68 kcal/mol for **1a**, **1p** and **1q**, respectively) to transfer the hydrogen of aldehyde group to the nitrogen of tertiary amine. Then, the obtained molecule containing carbonyl anion and ammonium cation (D state) could instantly lose CO due to lower

energy barrier (7.04, 1.80 and 2.34 kcal/mol for $1a_{ie}1p_{rel1}a_{ie}1q_{rel2}a_{ie}1q_{rel2}a_{ie}1q_{rel2}a_{ie}1q_{rel2}a_{ie}1q_{rel2}a_{ie}1q$



Scheme 4. Influence of acid on our photodecarbonylation (mechanistic studies-3). Isolated yield. PTSA = p-toluene sulphonic acid.



Scheme 5. Structural conditions of our photodecarbonylation (mechanistic studies-4). The reaction conditions were same as those in Scheme 2.

From Figure 3, we can see that under O-State, the substrates could also rapidly occur the photocyclization through the [1, 6]-H shift and the radical-radical coupling with low energy barriers. From Figure 2a, we can further see that, If H-State is more or less stable than O-State, the decarbonylation product (2 state) corresponding to H-State would also be correspondingly more or less stable than the undehydrated cyclization product (C state) corresponding to O-State. Thus, different initial conformations (H-State or O-State) indeed different photoreactions (photodecarbonylation cause or photocyclization). Intriguingly, whether the dominant conformation is H-State or O-State, the decarbonylation product (2 state) is less stable than the final dehydrated cyclization product (3 state), such as -8.92 vs -30.61, -8.90 vs -37.80, and 2.06 vs -25.56 kcal/mol for 1a, 1p and 1q, respectively (Figure 3). It suggested that acid which can accelerate the dehydration, could be utilized to prove the proposed

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conformational specificity. To be specific, since the substrates neutral to H-State and O-State were tolerated by both photodecarbonylation and photocyclization, the addition of acid could distinctly push the chemical equilibrium to the direction of photocyclization, improving the yield of cyclization product (Scheme 4). As expected, after 10% PTSA was added, the 60% decarbonylation product and trace cyclization product for 1p were turned to exclusive cyclization product in 70% yield. Considering solitary evidence does not stand, bromine (1ap), formonitrile (1aq) and methoxyl (1ar), were introduced into the benzene ring of 1p. Similarly, all the three substrates in the absence of acid produced decarbonylation products in good yields and cyclization products in trace yields, while in the presence of PTSA only afforded cyclization product in good yield. Meanwhile, the experiments on some special substrates (Scheme 5) suggested four aspects of structural conditions: (1) the hydrogen of aldehyde group should be polar (1ba) and irreplaceable (1bb-1bd); (2) the nitrogen of tertiary amine and the hydrogen of aldehyde group should be close enough (1be-1bh); (3) the tertiary amine cannot be replaced by secondary amines (1bi-1bj) which may form hydrogen bond with aldehyde group; (4) the nitrogen of tertiary amine cannot be replaced by carbon (1bk) or oxygen (1bl-1bn) which have less ability to take hydrion. Clearly, the four aspects point in one direction that the hydrogen of aldehyde group may be transferred to the nitrogen of tertiary amine through the [1, 4]-H shift.

Conclusions

In summary, based on the "conformational-selectivity-based" design strategy, we discovered a photodecarbonylation of aldehyde group which proceeds efficiently under operationally simple and very mild conditions. A wide variety of substrates are tolerated by this photodecarbonylation, and this methodology is noteworthy in that it does not require any catalysts. Furthermore, it also should be noted that since our photodecarbonylation can be easily achieved by introducing the tertiary amine into the ortho-position of aldehyde group, whether we can design a special tertiary amine which does not need to be introduced into the ortho-position of aldehyde group but could directly realize the photodecarbonylation by means of intermolecular reaction under mild conditions. Studies toward this direction are ongoing in our laboratories.

Conflicts of interest

There are no conflicts to declare.

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Catalyst-Free Photodecarbonylation: The decarbonylation easily achieved with visible light irradiation by introducing the tertiary amine into the *ortho*-position of aldehyde group.



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